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Preparation and spectra of some hexanuclear niobium halide cluster compounds

Peter Barry Fleming
Iowa State University

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PREPARATION AND SPECTRA OF SOME
HEXANUCLEAR NIOBIUM HALIDE CLUSTER
COMPOUNDS.**

**Iowa State University, Ph.D., 1968
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PREPARATION AND SPECTRA OF SOME
HEXANUCLEAR NIOBIUM HALIDE CLUSTER COMPOUNDS

by

Peter Barry Fleming

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

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Signature was redacted for privacy.

In Charge of ~~Major Work~~

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Ames, Iowa

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INTRODUCTION

In recent years the study of compounds containing metal-metal bonds has been enlarged tremendously. Within this area research on metal atom clusters of the type M_6X_{12} and M_6X_8 has also increased leading to an extension of the chemical and physical knowledge of these clusters.

This investigation has been concerned mainly with niobium clusters of the type Nb_6X_{12} . Through a study of the preparation of various complexes containing the niobium cluster it was hoped that the experimental chemistry of these clusters would become better defined. The clusters have also been studied by means of infrared and visible spectroscopy. In spite of the complexity of the species it was hoped that these studies would contribute to a better understanding of the electronic structure and bonding of these clusters.

Review of Previous Work

The early literature dealing with all cluster compounds has been summarized recently by Schäfer and Schnering (1). Other reviews (2,3,4) have discussed more specific areas of metal atom cluster compounds and because of this only the recent literature pertinent to this study of the niobium cluster compounds is discussed here.

Synthesis

Earliest preparations of the niobium cluster involved extracting the cluster into water as $\text{Nb}_6\text{X}_{12}^{2+}(\text{aq})$ and then crystallizing the hydrate, $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$. Harned et al. (5) used the above procedure on a product obtained from the reduction of niobium pentachloride with cadmium in vacuo at red heat. Allen and Sheldon (6), Robin and Kuebler (7), and Mackay and Schneider (8) also used the above method, and in addition the former two groups prepared small amounts of $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2 \cdot 7\text{H}_2\text{O}$.

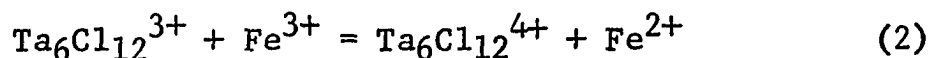
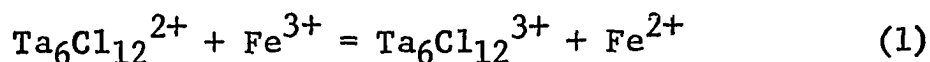
Recently, Fleming, Mueller, and McCarley (9) have obtained $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2 \cdot 8\text{H}_2\text{O}$ in up to 30% yield by aluminum reduction of niobium pentabromide in a gradient of 350/280^o. After extraction the hydrate was crystallized from neutral aqueous solution. In other work involving the hydrated cluster compounds Schäfer and Spreckelmeyer (10) have reported conditions for preparing $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_3 \cdot 7\text{H}_2\text{O}$ and $[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_3 \cdot 7\text{H}_2\text{O}$. In the case of the niobium compound, oxidation of a hydrochloric acid solution of $\text{Nb}_6\text{Cl}_{12}^{2+}(\text{aq.})$ with hydrogen peroxide and evaporation gives the 3+ hydrate¹. This compound is brown and

¹A notation where the cluster in a given oxidation state, $\text{Nb}_6\text{X}_{12}^{n+}$, is referred to by designating only $n+$ is established here.

paramagnetic (10) whereas the 2+ niobium chloride and bromide hydrates are dark green and diamagnetic (7,10,11).

Schäfer et al. (12) have prepared pure $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2$ by equilibrating niobium and Nb_3Cl_8 at temperatures in excess of 800° . In similar work Schäfer et al. (13) have found that $[\text{Nb}_6\text{F}_{12}]\text{F}_3$ can also be prepared by high temperature equilibration of niobium and niobium pentafluoride. Both $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2$ and $[\text{Nb}_6\text{F}_{12}]\text{F}_3$ are chemically unreactive at room temperature. No other anhydrous binary halide phases containing the Nb_6X_{12} unit are known at the present.

Coordination complexes of the niobium and tantalum clusters have only recently been reported. In studies leading to preparation of these new compounds, McCarley et al. (14) established the 4+ oxidation state of the $\text{Ta}_6\text{Cl}_{12}$ and $\text{Nb}_6\text{Cl}_{12}$ clusters. In a more detailed study, Espenson and McCarley (15) were able to establish the two one-electron oxidation reactions, Equations 1 and 2, in acidic solution.



Fleming, Mueller, and McCarley (9) have reported the preparation of $\text{K}_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ by equilibration of either $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2$ or a higher niobium chloride with potassium

chloride in a niobium tube at 300°. Fleming, Dougherty, and McCarley (16) have prepared $(\text{Et}_4\text{N})_x[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ ($X = 2,3$), $(\text{C}_6\text{H}_5)_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_4(\text{OH})(\text{H}_2\text{O})]$, $(\text{C}_6\text{H}_5)_3[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_5(\text{OH})]$, and $(\text{C}_6\text{H}_5)_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_5(\text{H}_2\text{O})]$ where Et_4N is tetraethylammonium and C_6H_5 is tetraphenylarsonium. The Et_4N salts are prepared by oxidizing a solution of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}]$ in ethanol saturated with hydrogen chloride with oxygen for the 3+ and chlorine for the 4+. The solid rapidly crystallizes upon addition of excess Et_4NCl . The 3+ tetraphenylarsonium complexes were obtained by addition of $\text{C}_6\text{H}_5\text{AsCl}$ to methanol-aqueous hydrochloric acid solutions of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}]$. In all cases the 3+ oxidation state is obtained by oxidation with oxygen. Progressively higher concentrations of hydrochloric acid were used to obtain the complexes in the above order. The 3+ complexes were all paramagnetic and the 4+ complexes diamagnetic.

Mackay and Schneider (8) reported the preparation of the complexes $(\text{Et}_4\text{N})_x[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ ($X = 2,3,4$). When $X = 2,3$ the method of preparation was nearly identical to that reported above (16) and when $X = 4$ a similar reaction was carried out under nitrogen. The 3+ complex was paramagnetic ($\mu_{\text{eff}} = 1.615 \text{ B.M.}$) and the 4+ diamagnetic where an effective

moment of 0.47 B.M. was attributed to 3+ impurity.

Mackay (17) also reports preparing the following complexes: $(\text{Et}_4\text{N})_2[(\text{Nb}_6\text{Cl}_{12})\text{X}_4(\text{EtOH})_2]$ ($\text{X} = \text{Cl}, \text{Br}$), $[(\text{Nb}_6\text{Cl}_{12})(\text{DMSO})_6](\text{ClO}_4)_2$, $(\text{Et}_4\text{N})_4[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]$, and $(\text{PyCH}_3)_4[(\text{Nb}_6\text{Cl}_{12})\text{I}_6]$ where $\text{PyCH}_3 = \text{N-methylpyridinium}$ and $\text{DMSO} = \text{dimethylsulfoxide}$. The first two complexes were prepared simply by refluxing $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}]$ in ethanol until it was dissolved, adding excess Et_4NX , and filtering to isolate the readily precipitated product. The DMSO adduct was prepared by adding silver perchlorate to ethanolic $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}]$, removing the silver chloride, and precipitating with DMSO. The last two complexes were prepared in a manner similar to $(\text{Et}_4\text{N})_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$. One tantalum complex, $(\text{Et}_4\text{N})_3[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]$, was reported by Mackay (17) to have been obtained in the same manner as the analogous niobium complex.

Meyer (18) has reported a more complete series of tantalum halide cluster complexes, viz. $(\text{Et}_4\text{N})_n[(\text{Ta}_6\text{Cl}_{12})\text{X}_6]$ ($n = 2, 3$ for $\text{X} = \text{Cl}$ and $n = 2$ for $\text{X} = \text{Br}$), $(\text{Et}_4\text{N})_2[(\text{Ta}_6\text{Br}_{12})\text{X}_6]$ ($\text{X} = \text{Cl}, \text{Br}$), and $(\text{As}_4\text{O})_2[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]$. All of the above 4+ complexes were obtained by saturating an ethanolic solution of $\text{Ta}_6\text{X}_{12}^{2+}$ with the appropriate hydrogen halide, oxidizing with elemental halogen, and concentrating the solution after

adding excess cation halide. The 3+ tantalum chloride cluster complex was made by starting with a solution of $[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol and following the above procedure with the rigorous exclusion of air. The 3+ bromide complex could not be made (18). The complex $\text{K}_4[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]$ was also obtained by Meyer (18) by heating stoichiometric quantities of tantalum pentachloride, potassium chloride, and aluminum in a sealed Vycor tube in a gradient of $540/400^\circ$ (upper end) for five days. The product was contaminated with KAlCl_4 .

In further recent work a series of complexes of the niobium chloride cluster with oxygen donor ligands has been reported by Field and Kepert (19). The complexes $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2\text{L}_4$, were prepared as follows: for $\text{L} = \text{DMSO}$ and DMF (dimethylformamide) a solution of $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ in the ligand was treated with a small volume of isopropanol to precipitate the solid; for $\text{L} = \text{As}_2\text{O}_3$ and P_2O_5 the ligand in ethanol was mixed with ethanolic $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ and the solution evaporated to dryness; for $\text{L} = \text{C}_5\text{H}_5\text{NO}$ the compound could readily be precipitated from an ethanol mixture made as above.

Structure determinations

Vaughan et al. (20) first demonstrated that the intensely colored solutions of lower niobium and tantalum halides contained discrete octahedra of metal atoms. Their studies on concentrated ethanol solutions of $[M_6X_{12}]X_2 \cdot 7H_2O$ by diffuse x-ray scattering showed cluster ions containing regular octahedra of metal atoms with $d_{M-M} = 2.85$ ($Nb_6Cl_{12}^{2+}$), 2.88 ($Ta_6Cl_{12}^{2+}$), and 2.92A ($Ta_6Br_{12}^{2+}$).

Burbank (21) has since obtained single crystal data on $[Ta_6Cl_{12}]Cl_2 \cdot 7H_2O$. The Ta_6 cluster is in the form of a tetragonal bipyramid with the long apex-apex distance being 0.98A longer than the waist diagonal. The Ta-Ta distances vary from 3.27 to 2.63A and all of the tantalum atoms are terminally coordinated suggesting a formulation, $[(Ta_6Cl_{12})Cl_2(H_2O)_4] \cdot 3H_2O$, where the uncoordinated water molecules lie in layers between layers of clusters.

Schäfer et al. (12) have shown by single crystal x-ray studies that $[Nb_6Cl_{12}]Cl_2$ contains tetragonally compressed Nb_6 units. The four basal Nb-Nb distances are 2.95₅A whereas the base to apex Nb-Nb distances are 2.89₅A. The formula is best represented as $[Nb_6Cl_{10}^i Cl_{2/2}^{i-a}] Cl_{2/2}^{a-i} Cl_{4/2}^{a-a}$ where i is an inner cluster chloride, $i-a$ is an inner chloride weakly bound

to another cluster, a-i is a weakly bound chloride from another cluster, and a-a is a normal bridge bonded chloride. Each niobium cluster is, then, completely coordinated by chloride ions.

$[\text{Ta}_6\text{I}_{12}]\text{I}_2$ has been found to be isostructural with $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2$ (22). The Ta_6 cluster is tetragonally compressed with basal Ta-Ta distances of ca. 3.08Å and the base to apex distance ca. 2.80Å. In the case of $[\text{Nb}_6\text{F}_{12}]\text{F}_3$, however, Schäfer et al. (13) have found the metal cluster to be a regular octahedron with $d_{\text{Nb-Nb}} = 2.80\text{Å}$. This singular example of a fluoride cluster compound is formulated as $[\text{Nb}_6\text{F}_{12}]\text{F}_{6/2}^{\text{a-a}}$. The inertness of the compound reflects its polymeric nature.

Bonding and physical measurements

Sheldon (23) discussed the bonding in $[(\text{Mo}_6\text{X}_8)\text{Y}_6]^{2-}$ cluster complexes in terms of $sp^3d_{x^2-y^2}$ hybrid orbitals used for Mo-X bonding and $d_{xz,yz}$ orbitals for Mo-Mo bonding along the octahedron edges. The remaining molybdenum electrons were considered to occupy the remaining metal d orbitals. Gillespie (24) extended Sheldon's approach by considering the repulsion arising between the Mo-X bond electron pairs. He arrived at a description which utilized all the molybdenum

electrons in the bonding but resulted in bent localized Mo-X bonds. A similar situation arises for the M_6X_{12} clusters. In view of recently obtained physical data the above descriptions are not very useful.

A molecular orbital treatment of the bonding in the $M_6X_{12}^{2+}$ and $M_6X_8^{4+}$ clusters was first proposed by Duffey (25) and Crossman et al. (26). Parametric equations were developed for the energy levels arising in each case from hybrid metal orbitals with the result that the chosen bonding orbitals for each cluster were just filled by the available electrons.

Cotton and Haas (27) used an approach similar to that of Crossman et al. (26) to calculate the relative energies of the molecular orbitals arising from four metal d orbitals on each atom ($d_{x^2-y^2}$ or d_{xy} was considered to be used on bonding only to halogens in the $M_6X_{12}^{2+}$ and $M_6X_8^{4+}$ clusters respectively). Metal-halogen interactions were excluded from this calculation. The bonding orbitals for the $M_6X_{12}^{2+}$ cluster in order of increasing energy were a_{1g} , t_{1u} , t_{2g} , and a_{2u} .

Robin and Kuebler (7) have used the LCAO-MO approach including metal-halogen interactions to obtain a relative ordering of one electron levels for $Nb_6Cl_{12}^{2+}$. In order to complete their scheme experimental electronic spectra were

employed to obtain the orbital ordering. The result, then, was consistent with their experimental data. It has since been shown by a comparison of spectra obtained by Espenson and McCarley (15) to Robin and Kuebler's data that their reported $Ta_6X_{12}^{4+}$ was indeed $Ta_6X_{12}^{3+}$. In addition a tetragonal distortion of the Ta_6 cluster and a resulting trapping of integral valence on the metal atoms was proposed to rationalize the tantalum cluster spectra. Coulomb repulsion forces were invoked as providing an internal mechanism for the distortion. This mechanism would lead to a tetragonal compression in the $4+$ cluster and a tetragonal elongation in the $2+$ cluster. Kettle (28) has pointed out that if both the metal-metal bonds and metal-halogen sigma bonds in $Nb_6X_{12}^{2+}$ and $Mo_6X_8^{4+}$ are considered the two structures are isoelectronic.

Mackay (17) has used the available molecular orbital calculations in conjunction with new spectral and magnetic data to obtain a reordering of the cluster molecular orbitals. A scheme consistent with his spectral data resulted. An important electron spin resonance experiment was also reported by Mackay and Schneider (8) in which they obtained a symmetric resonance with all but six of the expected fifty-five hyperfine lines for an electron delocalized over the Nb_6 unit

observed. The calculated hyperfine interaction constant was ca. one sixth of that found in the Nb(IV) complexes, $\text{NbCl}_5(\text{OCH}_3)^{2-}$ and NbCl_6^{2-} . This result is used as support for using d orbitals in the metal-metal bonding. Mackay and Schneider (8) conclude by agreeing with the general approach of Cotton and Haas (27) and especially by assigning the a_{2u} orbital as the top filled orbital in the 2+ and 3+ clusters.

Allen and Sheldon (6) have reported electronic spectra for $[\text{M}_6\text{X}_{12}]\text{X}_2 \cdot 7\text{H}_2\text{O}$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}$) in water and aqueous base solutions and in the solid. The eight bands reported were all assigned as metal-metal transitions according to the scheme of Cotton and Haas (27). Robin and Kuebler (7) obtained electronic spectra of a series of compounds similar to that of Allen and Sheldon (6) in ethanol at room and low temperature. They proposed two metal-metal transitions on the basis of small energy shifts on changing from chloride to bromide. Mackay (17) obtained spectra on many of the compounds prepared in his work and discussed the band assignments in relation to proposed energy level diagrams. Field and Kepert (19) were able to propose a spectrochemical series for their ligands and in addition discussed band assignments in terms of the orbital ordering.

Infrared spectra have been obtained by Boorman and Straughan (29) on some tantalum and niobium compounds. Generally, the compounds studied contained the $M_6X_{12}^{2+}$ ion with a variety of coordinated anions and neutral ligands. Their conclusion was that infrared spectroscopy may be useful in identifying the cluster. In a more detailed study Mackay (17) has obtained and analyzed the vibrational spectra of anions of the type $[(Nb_6Cl_{12})L_6]^{n-}$ and $[(Mo_6X_8)L_6]^{n-}$ where L was generally a uninegative anion. The niobium cluster spectra were assigned as either metal-inner chloride, metal-terminal chloride, or metal-metal modes. Five bands in the region $350-140\text{ cm}^{-1}$ were exhibited by the clusters including one at about 140 cm^{-1} assigned as a metal-metal mode. Meyer (18) has examined the vibrational spectra of the tantalum cluster compounds and reported qualitative band assignments. A one to one correspondence in bands between the 2+, 3, and 4+ oxidation states was found except that one band appeared to split in the 2+ and 4+. Neglecting the split band, then, five bands are found in the tantalum as in the niobium. Field and Kepert (19) have assigned the Nb-O stretch at ca. 430 cm^{-1} from their studies of the niobium chloride cluster coordinated by oxygen donors.

EXPERIMENTAL

Materials

In this work it was necessary to handle all niobium(V) halides and other starting materials in the absence of air. A drybox maintained with an argon atmosphere and dewpoint of less than -55° was used for storing and manipulating air sensitive compounds. Reactions involving the above types of compounds were generally carried out in evacuated Pyrex, Vycor, or niobium containers after the necessary preliminary steps had been carried out in the drybox and on the vacuum manifold.

Niobium

The niobium metal used in this work was supplied by E. I. duPont de Nemours and Co. in the form of high purity pellets. Niobium tubing (3/4 in.) was obtained from Fansteel Metallurgical Corp. and was then fabricated into reaction tubes of a desired length. These tubes were charged in the drybox and then after transportation in an argon filled bottle, a top was sealed in place in vacuo by electron beam welding.

Halogens

Chlorine was obtained in lecture bottles and used without purification. Bromine was reagent grade and was prepurified

for the preparation of niobium(V) bromide by distillation from phosphorous pentoxide in vacuo.

Hydrogen halides

Hydrogen chloride and hydrogen bromide were obtained in lecture bottles and were generally used without purification. However, in preparing solutions of the $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$ anion for spectral study as will be discussed later an outgassing and purification procedure was used on the hydrogen chloride. The lecture bottle was first outgassed directly by cooling with liquid nitrogen and evacuating to ca. 10^{-4} torr. The hydrogen chloride was then vacuum distilled into a previously outgassed solution of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}]$ in ethanol to remove any remaining oxygen and then used directly from this solution.

Organic solvents

All nonaqueous solvents were of reagent or spectro grade. In some instances it was necessary to use anhydrous and outgassed solvents. Absolute ethanol and acetone were outgassed by evacuation at room temperature to remove most of the dissolved gases and then evacuation to ca. 10^{-5} torr at the freezing point. The solvents were then vacuum distilled into flasks containing Linde 3A Molecular Sieves and used as needed.

Analytical Procedures

Solid samples were handled in one of three ways. Hydrolysis of a sample with ammonia followed by acidification of the solution with nitric acid generally allowed accurate determination of niobium and halogen. This method was the only reliable one for obtaining both halogen and metal when the sample contained halogens other than chloride. The "H-tube" method of Schäfer and Dohmann (30), which utilized oxidation of the sample with nitric acid, gave excellent results for chloride compounds, although for an unknown reason was not effective for bromides. The "H-tube" method was used whenever possible because of its simplicity and precision. When only niobium was determined the sample could be weighed directly into a tared crucible, oxidized to the oxide with nitric acid, dried, and ignited.

Teflon or polyethylene labware was used for fluoride containing samples. The analytical methods employed on solutions used to obtain spectra will be discussed in a later section.

Niobium

Niobium was always determined gravimetrically as the oxide, Nb_2O_5 . In the hydrolysis method a hydrous oxide is

obtained by filtration of the acid solution. Ignition to Nb_2O_5 is effected by charring the filter paper and then heating at $600\text{-}700^\circ$. In the other methods the oxide obtained can be placed directly in the muffle furnace.

Halogens

Halogens were determined gravimetrically as the silver halide or by potentiometric titration with a standard silver nitrate solution. Note that for samples analyzed by the "H-tube" method silver chloride is obtained as one product and this can be weighed after drying. For samples containing both chloride and bromide the total halide was precipitated and weighed as silver halide. The weight of silver halide was then compared with that expected for specific samples.

Fluorine was determined by the Ames Laboratory Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa.

Carbon and hydrogen

These elements 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. Samples were exposed to copper $K\alpha$ radiation for twenty to thirty hours.

Infrared spectra

Infrared absorption spectra were measured by the Ames Laboratory Spectrochemistry Group, Iowa State University of Science and Technology, Ames, Iowa. Samples were generally submitted as solids which were subsequently milled with nujol. In the cases where air sensitive compounds were measured the samples were milled in the drybox and sealed between polyethylene in a special cell constructed by the Ames Laboratory Shop. All far-infrared spectra were obtained with polyethylene windows. Spectra were obtained on a Beckman IR-7 spectrophotometer in the region $4000-600\text{ cm}^{-1}$ and on a Beckman IR-11 spectrophotometer in the region $800-42\text{ cm}^{-1}$.

Electronic Spectra

Solid state spectra

Diffuse reflectance spectra of solid compounds were measured from $50000-8550\text{ cm}^{-1}$ on a Beckman DU spectrophotometer

fitted with a Beckman 2580 reflectance attachment. Samples were ground to fine powders and diluted with either magnesium carbonate or an alkali metal halide containing the same halogen as that in the compound. The powdered mixture was loaded into a special metal cell equipped with an air tight fused quartz window so that air sensitive compounds could also be measured. A similar cell loaded with diluent was used as a reference.

Potassium chloride wafer spectra were measured on a Cary Model 14 recording spectrophotometer from ca. 40000-4000 cm^{-1} . Thin wafers were made by pressing an intimate mixture of the compound and potassium chloride for ca. 1 hour at 40,000 p.s.i. Spectra on the wafers were obtained with an air reference and as with the reflectance spectra at room temperature.

Solution spectra

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 baseline was recorded for each spectrum so that accurate absorbance values could be obtained at any desired wavelength.

Cryostat for low temperature spectra

In order to aid in resolving the complex electronic spectra of the cluster species into components it was decided to measure their spectra at low temperatures in solution. A cryostat for cooling spectrophotometer cells was designed for the above purpose.

The cryostat consisted of a stainless steel dewar container mounted on a brass plate which was machined to fit the Cary 14 spectrophotometer cell compartment. A hollow tube which was mounted in the center of the dewar continued through the bottom of the dewar as a bored-out copper rod so that it extended down into the instrument light path. A window (5/8" x 7/8") was then cut through the copper rod so that it was positioned in the instrument light path. The bore in the copper rod was fitted with a copper spring so that a 10 mm. spectrophotometer cell would be positioned directly in the light beam. To complete the design a larger diameter brass tube fitted with two removable quartz windows was placed as a jacket around the copper rod. This outer jacket could be bolted to the underside of the brass plate cell compartment cover. With the above arrangement the dewar and bottom jacket could be evacuated through a valve on the top of the

dewar. The inner copper rod and cell containing the solution then could be maintained at low temperature without condensation of moisture. A spectrophotometer cell could be loaded into the cryostat from the bottom or top.

Temperature

Generally it was attempted to cool a solution to near the freezing point of the solvent. A solution was cooled by filling the dewar with a melting slush of the solvent in question and allowing the spectrophotometer cell to cool for at least one and one-half hours. This time allowed proper cooling as determined in several measurements of the cell temperature with a thermocouple. In each case a thermocouple attached to the outside of a sealed cell but not in contact with the copper tube registered a temperature only a few degrees higher than the solvent melting point after one and one-half hours.

Solution preparation

The preparation of solutions used for spectral measurements was basically the same whether the measurements were made at room or lower temperature. In fact most solutions measured at low temperature were also measured at room temperature.

For low temperature measurements, however, it was necessary to contain the solution in a hermetically sealed spectrophotometer cell so that when the cryostat was evacuated solvent loss did not occur. In many cases a cluster compound was simply dissolved in the appropriate solvent. After loading a cell fitted with a quartz to Pyrex graded seal, the cell was connected to the vacuum manifold, cooled, and sealed off.

In some cases measurements on a cluster species in absolute ethanol saturated with hydrogen chloride were made. For the 3+ and 4+ oxidation states in the niobium chloride cluster system, $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in ethanol in the air and this solution was saturated with hydrogen chloride and oxidized with oxygen or chlorine respectively. When qualitative spectrophotometric verification of the correct oxidation state was completed the solution was poured into a cell and sealed off as discussed above. Note that prior to sealing the cell saturation with hydrogen chloride was insured by distilling hydrogen chloride into the cell in vacuo and then allowing any excess hydrogen chloride to bubble out of the solution so that approximately one atmosphere of hydrogen chloride remained over the solution at room temperature.

The above procedure was also carried out in preparing

solutions of 2+ cluster except that all manipulations were done in vacuo and prepurified hydrogen chloride as discussed previously was used. These precautions were necessary owing to the extremely rapid oxidation of 2+ cluster by oxygen in the presence of high chloride concentrations.

Solvents

Certain criteria were established to allow selection of proper solvents. First, a solvent should have a wide absorption free range, i.e., the ultra violet cut off should be as close to $50,000 \text{ cm}^{-1}$ as possible, and the solvent should be clear in the near infrared. Second, the integrity of an anionic cluster species, $[(M_6X_{12})Y_6]^{n-}$, should be preserved over at least a day. Third, a solvent should have a low freezing point so that a significant decrease in the population of excited vibrational states of the cluster occurs. Fourth, maximum concentration of the cluster species should be near 10^{-3} M . Two solvent systems were found that satisfied all four of the above, viz., ethanol saturated with hydrogen chloride (m.p. of pure ethanol $\approx -115^\circ$) and propionitrile (m.p. = -92°). Acetone (m.p. = -95°) was found to be an excellent solvent for measurements in the visible and near infrared regions of the spectrum. Several other solvents were

used for obtaining room temperature spectra, viz., acetonitrile, dimethyl sulfoxide, nitromethane, and nitroethane.

Analysis of solutions

In order to obtain extinction coefficients from the recorded absorbance versus wavelength data it was necessary to obtain an accurate molar concentration of cluster in the solution. Chemical analysis on most of the solutions was accomplished by more than one method. Samples for analysis were taken as aliquots of a solution prior to loading into a spectrophotometer cell, or in the case of the more concentrated solutions ($\sim 10^{-3}M$) aliquots of the solution actually measured were analyzed. The three methods used were as follows: 1) the solution was hydrolyzed with ammonia and then analyzed for niobium gravimetrically as discussed previously, 2) solutions were submitted to the Ames Laboratory Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa which determined niobium spectrophotometrically in concentrated sulfuric acid solution, 3) solutions in which the cluster species was unstable to oxidation or disproportionation to solid products were formed in nitric and sulfuric acid and submitted as concentrated sulfuric acid solutions of niobium(V) for spectrophotometric analysis as

above.

Molar concentrations obtained by these methods were generally in good agreement, and additionally, generally agreed with the concentration calculated from the weight of material used to prepare the solution. This latter estimation, of course, could only be made when a pure solid compound was used to make a solution.

Data processing

Since the recorded optical spectra of the cluster species were quite complex and consisted of several regions containing one or more shoulders, a resolution of the spectra into Gaussian error curve components was carried out in some cases. In order to facilitate resolution of the spectra a computer program was developed by the Ames Laboratory Computer Services Group, Iowa State University of Science and Technology, Ames, Iowa which utilized components defined by Equation 3 (31) to fit the experimental spectra.

$$\epsilon = \epsilon_0 e^{-\frac{(\nu - \nu_0)^2}{\theta^2}} \quad (3)$$

where: ϵ = extinction coefficient in ℓ mole⁻¹ cm⁻¹,

ϵ_0 = extinction coefficient at the absorption maximum,

ν = wavenumber in cm⁻¹,

ν_0 = wavenumber at the absorption maximum.

The quantity θ is related to δ , the band half-width at half-height according to Equation 4.

$$\theta = \delta / \sqrt{\ln 2} \quad (4)$$

The program used here made use of a least squares procedure to obtain a best fit of calculated Gaussian components to the experimental data. In order to operate, wavelength and absorbance data at appropriate intervals were used as input for the experimental spectra. A somewhat arbitrary decision as to the number of individual spectral bands in a certain region then had to be made and used as input so that a given region of the spectrum was resolved only into a prescribed number of components. In order to accomplish this the parameters, ν_0 , ϵ_0 , and θ (see Equations 3 and 4) were estimated for input, and then in fitting the spectrum these parameters were varied two at a time until an increment of 0.1% in each one did not improve the fit of calculated to experimental spectra.

The computer output consisted of the three parameters, ν_0 , ϵ_0 , and θ , for each component band and the resultant ϵ for each input wavelength. Through repeated use of the program each spectrum could be separated into its major components.

Synthesis

Niobium(V) halides

Niobium(V) halides were prepared by combination of the elements at 400-450° in an evacuated tube. Amounts of up to 200 g. were made each time, and they were stored in the drybox for further use.

Anhydrous binary niobium cluster halides

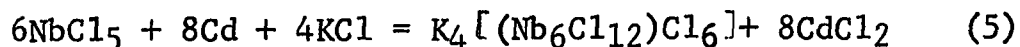
The compounds $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2$ and $[\text{Nb}_6\text{F}_{12}]\text{F}_3$ were prepared by methods similar to those previously reported, (12) and (13), respectively. In the case of the fluoride, niobium pentafluoride (Ozark Mahoning Corp.) was purified by slow sublimation and then loaded into a niobium tube with some niobium granules. After sealing the niobium tube in vacuo by electron beam welding, the mixture was equilibrated at a temperature in excess of 500° for ca. one week. It was found that the equilibration could be carried out at up to 800° with the same golden brown powder of $[\text{Nb}_6\text{F}_{12}]\text{F}_3$ resulting.

Aquo(dodeca- μ -halo-hexaniobium) dihalides

The hydrated cluster compounds were used as starting materials in preparing many of the cluster coordination complexes. Several reactions which provide cluster containing products have been previously discussed (5-9), and the

isolation of the octa hydrates, $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ and $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2 \cdot 8\text{H}_2\text{O}$, has been described (9). In the course of this work additional cluster providing reactions were found, and they are discussed below in addition to some new hydrates.

Reduction in molten halides In a reaction in the chloride system, 20 grams of niobium(V) chloride, a slight stoichiometric excess of cadmium metal (Equation 5) and 50-60 grams of lithium chloride-potassium chloride eutectic mixture (m.p. $\sim 355^\circ$) containing a small excess of potassium chloride were sealed in a Pyrex tube with a magnetic stir bar.



The mixture was heated on a stir plate with a heating tape at 360° for ca. 44 hours. After cooling the tube was opened in the air and the $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ obtained in the usual manner (9). The yield was 80% of the calculated amount.

In the bromide system the above reaction was carried out with the modifications described below. Fifteen grams of niobium(V) bromide, aluminum, and lithium bromide-potassium bromide eutectic (m.p. $\sim 320^\circ$) were used as reactants. The mixture was heated as above at ca. 400° for ca. 20 hours prior to the isolation of $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2 \cdot 8\text{H}_2\text{O}$ from the product as previously described (9). In later reactions it was found that

the reactants could be mixed by shaking the reaction tube with a mechanical shaker. The yields for two reactions were 55 and 48% of that calculated for $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2 \cdot 8\text{H}_2\text{O}$.

$[\text{Nb}_6\text{Cl}_{12}]\text{Br}_2 \cdot 7\text{H}_2\text{O}$ A solution of 5 grams of $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ in ca. 3 liters of water was trickled through a column of strongly basic anion exchange resin (Amberlite IRA-400) in the bromide form. The resulting solution was made ca. 0.6M in hydrogen bromide and evaporated slowly at 30° to yield black crystals. The crystals were collected on a glass frit, washed with ether, and dried in vacuo.

Anal: Calcd. for $[\text{Nb}_6\text{Cl}_{12}]\text{Br}_2 \cdot 7\text{H}_2\text{O}$: Nb, 43.93; AgX (for one specific sample), 344.2 mg. Found: Nb, 43.97; AgX (for one specific sample), 351.1 mg.

$[\text{Nb}_6\text{Cl}_{12}]\text{F}_2 \cdot 8\text{H}_2\text{O}$ A solution of $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ in water was made ca. 0.6M in hydrogen fluoride and evaporated slowly to ca. one fourth of the original volume. At this point the solution was nearly colorless and black needles had crystallized on the bottom of the teflon beaker. The product was isolated on a glass frit, washed with ether, and dried in vacuo.

Anal: Calcd. for $[\text{Nb}_6\text{Cl}_{12}]\text{F}_2 \cdot 8\text{H}_2\text{O}$: Nb, 47.85; Cl,

36.52. Found: Nb, 47.94; Cl, 37.28 ± 0.15 [2]; Cl/Nb, 2.04.¹

Bis(n-propylammonium)hexachloro(dodeca- μ -chloro-hexaniobium)

This complex was prepared in a manner similar to that used for the $4+$ Et_4N^+ complex (16). The reaction solution containing a 3 mole excess of n-prNH₃Cl (n-propylammonium chloride) was evaporated to a point where it was ca. 0.4M in cluster and cooled at 0° for four hours to aid crystallization. The product was obtained as small black crystals on a glass frit by filtration.

Anal: Calcd. for $[\text{n-C}_3\text{H}_7\text{NH}_3]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$: Nb, 42.82; Cl, 49.03; C, 5.54; H, 1.54. Found: Nb, 42.11 ± 0.09 [2]; Cl, 47.47; C, 5.46 ± 0.11 [3]; H, 1.85 ± 0.14 [3]; Cl/Nb, 2.95.

Tris(n-propylammonium)hexachloro(dodeca- μ -chloro-hexaniobium)

This complex was also prepared by a method similar to that used previously for the $3+$ Et_4N^+ complex (16). In this case, though, pure oxygen gas was bubbled through the hydrogen chloride saturated cluster solution for 30 minutes to aid the oxidation. When the cluster oxidation state was determined

¹The results are listed as arithmetic averages of the number of analyses in brackets \pm the average deviation. When no deviation is given, only one analysis was done.

to be 3+ spectrophotometrically, the solution was added to a solution containing a 2.5 mole excess of n-prNH₃Cl in ethanol. This solution was then poured into a flask fitted with a filtering frit so that ethanol could be removed and crystallization allowed in vacuo. This precaution was felt advisable due to the much greater solubility of the n-propylammonium cluster complexes relative to those of tetraethylammonium, and hence longer exposure of the cluster to oxygen if the crystallization was carried out in the air. The solution, then, was concentrated in vacuo, resaturated with hydrogen chloride, and allowed to set overnight. The product was isolated on the frit by filtration, washed with two 50 ml. portions of chloroform in vacuo, and then vacuum dried to a dark olive powder.

Anal: Calcd. for [n-C₃H₇NH₃]₃[(Nb₆Cl₁₂)Cl₆]: Nb, 40.52; Cl, 46.39; C, 7.85; H, 2.20. Found: Nb, 40.41 ± 0.14 [2]; Cl, 46.18; C, 7.51 ± 0.01 [2]; H, 2.41 ± 0.05 [2]; Cl/Nb, 2.99.

Bis(n-propylammonium)hexabromo(dodeca-μ-chloro-hexaniobium)

A solution of [Nb₆Cl₁₂]Br₂·7H₂O in ethanol was saturated with hydrogen bromide and oxidized with bromine in the air. Subsequently a 6 mole excess of n-prNH₃Br was added, the solution was concentrated to ca. one-third its original volume, and then cooled at -25° for one hour. The product was iso-

lated on a frit as a black powder, washed with copious quantities of chloroform and ether, and dried in vacuo.

Anal: Calcd. for $[\text{n-C}_3\text{H}_7\text{NH}_3]_2[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]$: Nb, 35.23; C, 4.55; H, 1.27; AgX (for one specific sample), 360.4 mg. Found: Nb, 34.50; C, 4.92 ± 0.02 [2]; H, 1.46 ± 0.03 [2]; AgX (for one specific sample), 355.9; X/Nb, 3.01.

Bis(n-propylammonium)hexabromo(dodeca- μ -bromo-hexaniobium)

This preparation was carried out as above with the exceptions that $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2 \cdot 8\text{H}_2\text{O}$ was the starting cluster and the solution was concentrated to about one-half its original volume by vacuum distillation prior to resaturation with hydrogen bromide and overnight crystallization at 25° . The product was isolated as a brown powder in the air, washed with copious amounts of chloroform and ether, and dried in vacuo.

Anal: Calcd. for $[\text{n-C}_3\text{H}_7\text{NH}_3]_2[(\text{Nb}_6\text{Br}_{12})\text{Br}_6]$: Nb, 26.34; Br, 67.98; C, 3.40; H, 0.95. Found: Nb, 26.43; Br, 67.18; C, 2.97 ± 0.16 [4]; H, 1.11 ± 0.08 [4]; Br/Nb, 2.96.

Bis(tetra-n-butylammonium)hexabromo(dodeca- μ -bromo-hexaniobium)

This complex was prepared in a manner similar to the n-propylammonium complex above except that with the larger cation concentration of the solution was unnecessary. After

addition of excess tetra-n-butylammonium bromide to the ethanolic cluster solution crystallization was allowed to proceed overnight at 25^o. The product was isolated on a frit as black crystals and then dried in vacuo.

Anal: Calcd. for $[(n-C_4H_9)_4N]_2[(Nb_6Br_{12})Br_6]$: Nb, 22.47; Br, 57.99; C, 15.48; H, 2.93. Found: Nb, 22.84 \pm 0.03 [2]; Br, 56.87; C, 15.82 \pm 0.55 [3]; H, 2.60 \pm 0.05 [3]; Br/Nb, 2.90.

Bis(n-propylammonium)hexachloro(dodeca- μ -bromo-hexaniobium)

This preparation was carried out as above with the exceptions that the cluster solution was saturated with hydrogen chloride and oxidized by a 45 second chlorine flush. After adding a 4 mole excess of n-propylammonium chloride the solution was cooled to -10^o with a continuing hydrogen chloride flush for two hours to allow crystallization. The product was then isolated on a frit as fine black crystals, washed with a small amount of ethanol and larger quantities of chloroform and ether prior to drying in vacuo.

Anal: Calcd. for $[n-C_3H_7NH_3]_2[(Nb_6Br_{12})Cl_6]$: Nb, 30.15; C, 3.89; H, 1.09; AgX (for a specific sample), 299.8, 339.6 mg. Found: Nb, 30.98 \pm 0.20 [2]; C, 3.97 \pm 0.02 [2]; H, 1.18 \pm 0.06 [2]; AgX (for a specific sample), 293.4, 331.6 mg.

Bis(tetra-n-butylammonium)hexachloro(dodeca- μ -bromo-hexaniobium)

This compound was prepared in a manner analogous to that described above for the $n\text{-prNH}_3^+$ complex. The crystallization was allowed to proceed overnight at 25° yielding black crystals. The product was isolated on a frit and washed with chloroform and ether prior to vacuum drying.

Anal: Calcd. for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[(\text{Nb}_6\text{Br}_{12})\text{Cl}_6]$: Nb, 25.18; C, 17.35, H, 3.28. Found: Nb, 25.54; C, 17.50 ± 0.13 [2]; H, 3.50 ± 0.03 [2].

Tetrakis(tetraethylammonium)hexafluoro(dodeca- μ -chloro-hexaniobium)

A filtered solution of $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ in ethanol was made acidic with a small amount of hydrogen fluoride. To this solution, which was contained in a teflon beaker, a 20 mole excess of tetraethylammonium fluoride over that required to form the desired complex was added and the solution was evaporated to ca. 5% of its original volume. At this point precipitation of a product was noticed so the solution was cooled to 25° to allow more complete crystallization prior to isolating the product on a frit. The product was washed with large volumes of chloroform and then ether, and dried

to an olive powder in vacuo.

Anal: Calcd. for $[(C_2H_5)_4N]_4[(Nb_6Cl_{12})F_6]$: Nb, 34.46; Cl, 26.30; F, 7.05. Found: Nb, 33.13; Cl, 25.45; Cl/Nb, 2.01.

Due to a question on whether the cluster had been saturated with fluoride in the terminal positions the above procedure was repeated on the previous product. As shown by the analytical data the same product was probably obtained.

Anal: Found: Nb, 33.66; Cl, 24.95 ± 0.12 [2]; F, 6.18 ± 0.20 [5]; Cl/Nb, 1.94; F/Nb, 0.90.

Alkali metal hexachloro(dodeca- μ -chloro-hexaniobium) complexes

New complexes of the type $M_4[(Nb_6Cl_{12})Cl_6]$ (M = Li, Na) were prepared exactly as $K_4[(Nb_6Cl_{12})Cl_6]$ had been (9). Briefly, the synthesis involves charging a niobium tube with stoichiometric quantities of $[Nb_6Cl_{12}]Cl_2$ and the alkali metal chloride, sealing the tube off in vacuo, and equilibrating the tube in an evacuated quartz container at ca. 800° for a few days.

In a separate experiment designed to yield a proof of the composition of the lithium salt, $[Nb_6Cl_{12}]Cl_2$ was equilibrated with excess lithium chloride at ca. 800° for six days. This product was then extracted in vacuo with anhydrous ether

to remove the excess lithium chloride. The product was then vacuum dried and analyzed.

Anal: Calcd. for $\text{Li}_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$: Nb, 45.57; Cl, 52.16. Found: Nb, $47.40 \pm .28[2]$.

Although a chloride analysis was attempted using the "H-tube" technique it was not possible to completely oxidize the compound. This difficulty is indicative of the presence of niobium metal which would explain the high niobium result.

In a second experiment a niobium tube was charged with niobium pentachloride and lithium chloride, and then equilibrated at 800° for six days. The product was extracted with ether as above and an analysis performed.

Anal: Found: Nb, 45.54; Cl, 50.74; Cl/Nb, 2.92.

Tris(tetra-n-butylammonium)hexaiodo(dodeca- μ -chloro-hexaniobium)

A solution of $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ was made up in ethanol, filtered, and refluxed with excess tetra-n-butylammonium iodide. This solution was then cooled and filtered. After accidental introduction of water, however, the solution was evaporated to near dryness and the above procedure repeated after extraction of the residue with ethanol. Upon cooling successive batches of crystals were isolated on a frit. The

first batch of red-brown crystals was washed with chloroform and ether and then dried in vacuo. Succeeding batches consisted of chloroform soluble large black plates which upon standard analytical and infrared analysis were concluded to contain no niobium. The first batch of red-brown crystals were more promising.

Anal: Calcd. for $[(C_4H_9)_4N]_3[(Nb_6Cl_{12})I_6]$: Nb, 22.56; Cl, 17.22; I, 30.81; C, 23.31; H, 4.41. Found: Nb, 24.21 ± 0.38 [3]; Cl, 17.65 ± 0.91 [3]; I, 28.84; C, 21.63 ± 0.19 [2]; H, 4.03 ± 0.02 [2]; Cl/Nb, 1.91; I/Nb, 0.87.

Attempts were made to synthesize some other cluster complexes particularly the $Nb_6Br_{12}^{3+}$ containing complexes. Some of this work will be discussed in a later section.

RESULTS AND DISCUSSION

Synthesis

Hydrates

The isolation of cluster hydrates of the type $[\text{Nb}_6\text{X}_{12}]^n\text{Y}_2 \cdot 8\text{H}_2\text{O}$ where X is a halogen and Y is an anion (halogen or other) is fairly straightforward. There are two approaches which can be used when a compound where X is different than Y is desired. One, the terminal X group of the compound, where the terminal and inner halogens are the same, can be removed chemically by ion exchange or possibly other methods. Two, in a solution containing a cluster where X is the same as Y, excess of a new Y group can be added and then the usual crystallization carried out. The ion exchange procedure had previously been used to prepare sulfate derivatives of $\text{Ta}_6\text{Cl}_{12}^{n+}$ ($n = 2,4$) (14). In the case of the fluoride hydrate, $[\text{Nb}_6\text{Cl}_{12}]^n\text{F}_2 \cdot 8\text{H}_2\text{O}$, addition of hydrofluoric acid to the aqueous $[\text{Nb}_6\text{Cl}_{12}]^n\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ solution resulted in rapid crystallization.

Since the non-cluster halogen has been found to be coordinated to the cluster, as shown by Burbank (21) for $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$, the fluoride ion in this compound also is likely to be coordinated to the cluster. The far

infrared spectrum exhibited bands at 505(w) and 406(s,broad) cm^{-1} which are in the region where niobium-terminal fluoride bands are expected. The 406 cm^{-1} band may be partially due to coordinated water.

In the preparation of this compound, it was observed that it is less soluble in similar anion concentrations than the other hydrates.

$[\text{Nb}_6\text{Cl}_{12}]\text{F}_2 \cdot 8\text{H}_2\text{O}$ is nearly insoluble in water, insoluble in acetonitrile, rapidly soluble in DMSO and 2M aqueous hydrofluoric acid, and soluble in ethanol. This behavior differs from the other hydrated clusters which are soluble in water to greater than 10^{-3}M .

It should be pointed out that although the hydrate number has generally been found to be eight in this work and elsewhere (32), an error of \pm one H_2O per mole of compound should be considered as reasonable.

One difficulty that has been encountered in preparing 2+ hydrates is that in the presence of excess hydrohalic acid a slight air oxidation to the 3+ state occurs (10). Converse (11) has shown that the 2+ and 4+ niobium and tantalum clusters are diamagnetic. Thus the slight temperature dependence in the magnetic susceptibility of the hydrates can be

attributed to 3+ impurity, which probably is in the form $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_3 \cdot 7\text{H}_2\text{O}$ (10). It may be possible to obtain pure $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ by the addition of a large excess of hydrochloric acid which is known to rapidly precipitate the compound¹.

In one series of reactions a new route to obtaining cluster compounds was developed. It was found that cadmium or aluminum reduction of niobium(V) chloride or bromide, respectively, in a lithium halide-potassium halide eutectic melt gave good yields of octahydrate after water extraction of the crude product. There are several reasons why reduction in these melts is more effective than other methods (9). One, rapid stirring of the mixture results in good contact between the reducing metal and the dissolved niobium(V) halide. Two, the bromide reaction can be run for only a short time at ca. 400° which is below the temperature at which rapid disproportionation of $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2$ ² occurs (9). Three, the

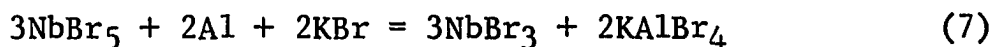
¹Koknat, F. W. Ames, Iowa. Studies on the preparation of niobium cluster hydrates. Private communication. 1967.

²Although $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2$ has never been isolated it is assumed for the purpose of discussion that it is the anhydrous species formed in many of the solid state reactions. Note especially that this species is not implied to exist in an ionic bromide melt.

cluster species formed in an ionic melt may be $[(\text{Nb}_6\text{X}_{12})\text{X}_6]^{4-}$ which then could be precipitated as a salt of the type $\text{M}_4[(\text{Nb}_6\text{X}_{12})\text{X}_6]$ (M = alkali metal). Anionic complex formation may stabilize the cluster in the melt. The best evidence of complex salt formation in the reactions (Equations 5 and 6) is that the product dissolves immediately in water, a behavior analogous to the $\text{M}_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ salts and opposite to $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2$. The chloride reaction (Equation 5) goes nearly to completion whereas the bromide reaction (Equation 6) only

$$18\text{NbBr}_5 + 16\text{Al} + 28\text{KBr} = 3\text{K}_4[(\text{Nb}_6\text{Br}_{12})\text{Br}_6] + 16\text{KAlBr}_4 \quad (6)$$

yields about 50% of the calculated amount of cluster. Powder pattern identification of niobium tribromide ($\text{NbBr}_{2.67}$ (Nb_3Br_8) - $\text{NbBr}_{3.03}$) (33) in the aluminum reduction product has been made, so a competing reaction (Equation 7) evidently occurs.



Anionic complexes

The preparation of complexes containing the 4+ cluster is relatively straight forward. Oxidation of the cluster is effected with elemental halogen identical to that desired as a terminal ligand, and saturation of the ethanolic cluster solution with terminal ligand is accomplished with the

appropriate hydrogen halide. In some cases the elemental analyses show a deficiency of halogen ($X/Nb < 3.0$) which is indicative of incomplete anation of the cluster.

If this was the case, however, it was felt that either a solvent or water molecule could occupy some fraction of the terminal coordination positions. No evidence from the infrared data was found to indicate the coordination of water, hydroxide, or ethanol to the cluster; for these ligands bands in the following regions were possible: ca. 420 cm^{-1} (Nb-O stretch) and 1600 cm^{-1} (H-O-H bending). Small discrepancies in the observed analytical data compared to calculated values can be explained by inclusion of about 1% of free alkyl ammonium halide in the product. Even the careful chloroform washings given the products may not have removed all of the excess cation halide.

The 4+ complexes are diamagnetic (11) and soluble in acetone, acetonitrile, propionitrile, nitromethane, nitroethane, and ethanol. The complexes are insoluble in water except that warming induces an apparent disproportionation (or reduction) to the 2+ cluster. The complexes are also soluble in DMSO but with reduction to the 3+ oxidation state (see discussion of spectra). The preparation of 3+ hexahalo

cluster complexes is more difficult than the 4+ complexes since the danger of over-oxidation is present. It was found that rapid one electron air oxidation of the 2+ cluster occurs in the presence of excess halide and that further oxidation is slower. The preparation of the 3+ hexachloro chloride complex is straightforward as explained in the experimental section.

Several attempts to prepare a derivative of $[(\text{Nb}_6\text{Br}_{12})\text{Br}_6]^{3-}$ were made without good success. The method of preparation was similar to that used for the chloride with the cluster being oxidized with oxygen until it had been estimated spectrophotometrically that the cluster oxidation state was 3+. At this point alkyl ammonium bromide was added and solvent removed in vacuo.

Two products with n-propyl ammonium as cation were obtained. Their electronic spectra in acetone indicated a mixture of $[\text{Nb}_6\text{Br}_{12}]^{3+}$ and 4+ cluster as did elemental analyses. These products were noted to fume (HBr) in air, a behavior not observed for the 4+ bromide cluster.

One separate experiment using tetra-n-butylammonium as the cation yielded a product which reacted with air after vacuum drying to evolve dense white fumes (HBr) and leave a

yellow residue (NbOBr_3). This was the most promising product obtained, and if handled in the absence of oxygen may have had a composition close to that of the desired complex. The use of tetra-n-butyl ammonium cation certainly allows for a more rapid crystallization.

Several attempts to prepare the complex $[\text{Et}_4\text{N}]_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ by the method used for the 3+ and 4+ complexes were made without successfully preventing oxidation. Oxidation of the cluster, presumably by oxygen, could not be prevented even though solutions were handled on the vacuum manifold. In one case a product approximating $[\text{Et}_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_4(\text{EtOH})_2]$ was obtained but not studied further.

Using a new approach to this problem the preparation of $(\text{Et}_4\text{N})_4[(\text{Nb}_6\text{Cl}_{12})\text{F}_6]$ was carried out using a procedure developed by Koknat¹ to prepare pure $(\text{Me}_4\text{N})_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$. In this type of reaction, as detailed in the experimental section, air oxidation is apparently prevented by the relative insolubility of the complex. This was especially evident in the case of the 2+ hexachloro chloride¹, but due to the teflon beaker and concentrated cluster solution precipitation was

¹Koknat, F. W. Ames, Iowa. Studies on the preparation of $[\text{Me}_4\text{N}]_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$. Private communication. 1967.

difficult to see for the hexafluoro chloride. The analytical data for this latter compound were low in all elements, but the ratios of halogen to niobium were reasonably good. This hexafluoro complex was soluble in ethanol but insoluble in acetone.

The synthesis of the anhydrous alkali metal complexes $M_4[(Nb_6Cl_{12})Cl_6]$ was straightforward. The chemical analysis of the lithium salt was not conclusive in proving the composition but in conjunction with the chemical properties the compound is assigned as $Li_4[(Nb_6Cl_{12})Cl_6]$.

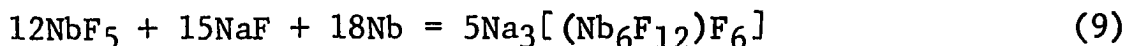
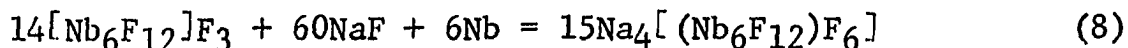
The lithium salt was found to rapidly dissolve in water, acetone, acetonitrile, and DMSO and to be insoluble in ether. In comparison to the other alkali metal complexes the following solubility trend in the above solvents appears to hold: $Li > Na > K$. A comment on the solubility of the lithium salt is in order. It was found that $Li_4[(Nb_6Cl_{12})Cl_6]$ that had been stored in the dry box was actually nearly insoluble in a variety of solvents. However, if the complex is allowed to stand in air for a short time prior to treating with a solvent the solution process is rapid. This procedure is similar to one used by Cotton and Mague (34) to solubilize Re_3Cl_9 . In this case the solubilization probably involves a partial

hydration of the lithium ion or cluster which is sufficient to lower the lattice energy relative to the solvation energy.

Inner fluoride complexes

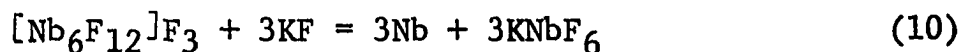
Other synthesis studies in this work were directed toward preparing complexes containing the fluoride cluster, Nb_6F_{12} . As has previously been found (13), the compound $[\text{Nb}_6\text{F}_{12}]\text{F}_3$ has strong intercluster fluoride bridge bonding and is chemically intractable. In view of these facts it was considered desirable to obtain a fluoride cluster in a form amenable to chemical and physical study. It was hoped that the differences between the fluoride and other halide ions would be manifested in obvious differences in cluster properties.

One approach was to attempt to prepare an alkali metal complex of the type, $\text{M}_n[(\text{Nb}_6\text{F}_{12})\text{X}_6]$ ($n = 3,4$), where X is a halogen, through use of reactions that have been proved in the chloride system (Equation 8 or 9). Note that the oxida-

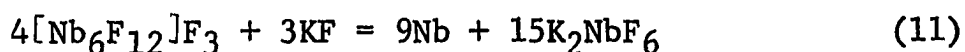


tion state of a new cluster product would not be certain a priori. A reaction was carried out according to the stoichiometry of Equation 8 by equilibrating the reactants for

six days at 600° in a sealed niobium tube. The black product appeared to be inert to water and only niobium metal could be identified in the product. A similar experiment with potassium fluoride yielded a product like the one above. A powder pattern of the product showed that KNbF₆ was a probable product and a pattern of the residue after water extraction indicated the presence of niobium. The probability of KNbF₆ being formed via a disproportionation (Equation 10) was concluded by comparing d-spacings calculated from single crystal data (35) with the pattern obtained and being able to find 40% of the KNbF₆ lines expected. A disproportionation



leading to a Nb(IV) complex would also be possible (Equation 11).

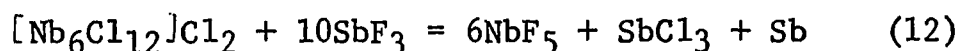


Several inner halogen exchange reactions were also carried out in an attempt to synthesize a fluoride complex. It has earlier been shown by Sheldon (36) that heating [Mo₆Cl₈]Cl₄ in molten lithium iodide or bromide for a short time resulted in a 50-80% yield of the exchanged cluster, [Mo₆X₈]X₄ (X = I, Br).

In one experiment, [Nb₆Cl₁₂]Cl₂ and an excess of a

45:45:10 mole ratio KF:LiF:NaF mixture (m.p. = 454°) were heated at 550° in vacuo in a platinum crucible for two hours. The product was a black insoluble mass. Powder x-ray analysis indicated the presence of niobium metal and other unidentified products. It was concluded that in the basic fluoride melt the cluster disproportionated as described above.

A reaction of $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2$ and excess antimony trifluoride in vacuo at 325° for ca. fourteen hours yielded a gray product and a white sublimate. The sublimate definitely contained antimony trichloride and, of course, antimony trifluoride. Elemental antimony was found in the solid residue. After subtracting the lines of antimony, the x-ray powder pattern contained only a few unassigned weak lines. Apparently, if any niobium containing product was in the residue it was amorphous. The conclusion here is that exchange of fluoride for chloride did take place, but subsequent oxidation by SbF_3 produced a volatile higher niobium fluoride which may have been removed in the sublimate. A plausible reaction scheme is given by Equation 12.



One other exchange reaction was attempted, where it was hoped that the intercluster fluoride bridges in $[\text{Nb}_6\text{F}_{12}]\text{F}_3$

might be broken and an anionic complex of the type $[(\text{Nb}_6\text{F}_{12})\text{Cl}_6]^{n-}$, formed. In this case $[\text{Nb}_6\text{F}_{12}]\text{F}_3$ was heated in a LiCl-KCl eutectic melt for a short time and the product extracted with water. The visible spectrum in water was characteristic of the $\text{Nb}_6\text{Cl}_{12}^{2+}$ (aq.) ion. After exchange of free halide for $\text{SO}_4^{=}$ via an ion exchange resin analysis of the solution showed Cl/Nb = 1.95. The conclusion was that the fluoride cluster was transformed to the chloride cluster in the melt.

The result of the work designed to yield a cluster with inner fluoride ions is that it is not feasible to prepare such a cluster in any form other than $[\text{Nb}_6\text{F}_{12}]\text{F}_3$. In order to break up the intercluster bridging it is necessary to use a strongly basic solvent. Unfortunately all solvents tried led to products other than the desired $\text{Nb}_6\text{F}_{12}^{n+}$ derivatives. The stoichiometry of these reactions has not been established unequivocally so that the possibility of a novel lower niobium fluoride complex still exists.

Electronic Spectra

Method and cluster species

Optical spectra on some $\text{M}_6\text{X}_{12}^{n+}$ cluster species were measured as explained in the experimental section. The measurement of these spectra was undertaken in an attempt to

resolve the differences in spectra obtained in other studies (7,17,19) and the resulting confusion in assignment of these spectra. Logical development of the problem involved assuming that the spectra obtained could be attributed to a given species, in general $[(\text{Nb}_6\text{X}_{12})\text{Y}_6]^{n-}$, and then using the techniques of low temperature measurement and Gaussian resolution to locate the spectral bands.

To facilitate the discussion of the spectra and deductions about the electronic structure of the M_6X_{12} cluster, this section has been subdivided into several parts.

Certain aspects of the experimental measurements deserve comment as well as the behavior of the species, $[(\text{Nb}_6\text{X}_{12})\text{Y}_6]^{n-}$, in various solvents. The measurement of spectra at low temperatures was found to be helpful in resolving weak bands in the 30, 15-20, and 6-10 kK regions of the spectra. An illustration of this effect is shown in Figure 1. The data obtained from these measurements were then more amenable to resolution into Gaussian components than room temperature data, and in fact a better visual estimation of band positions could be made. Resolution of some typical spectra is shown in Figures 2 and 3.

In order to discuss the spectra of the cluster in its

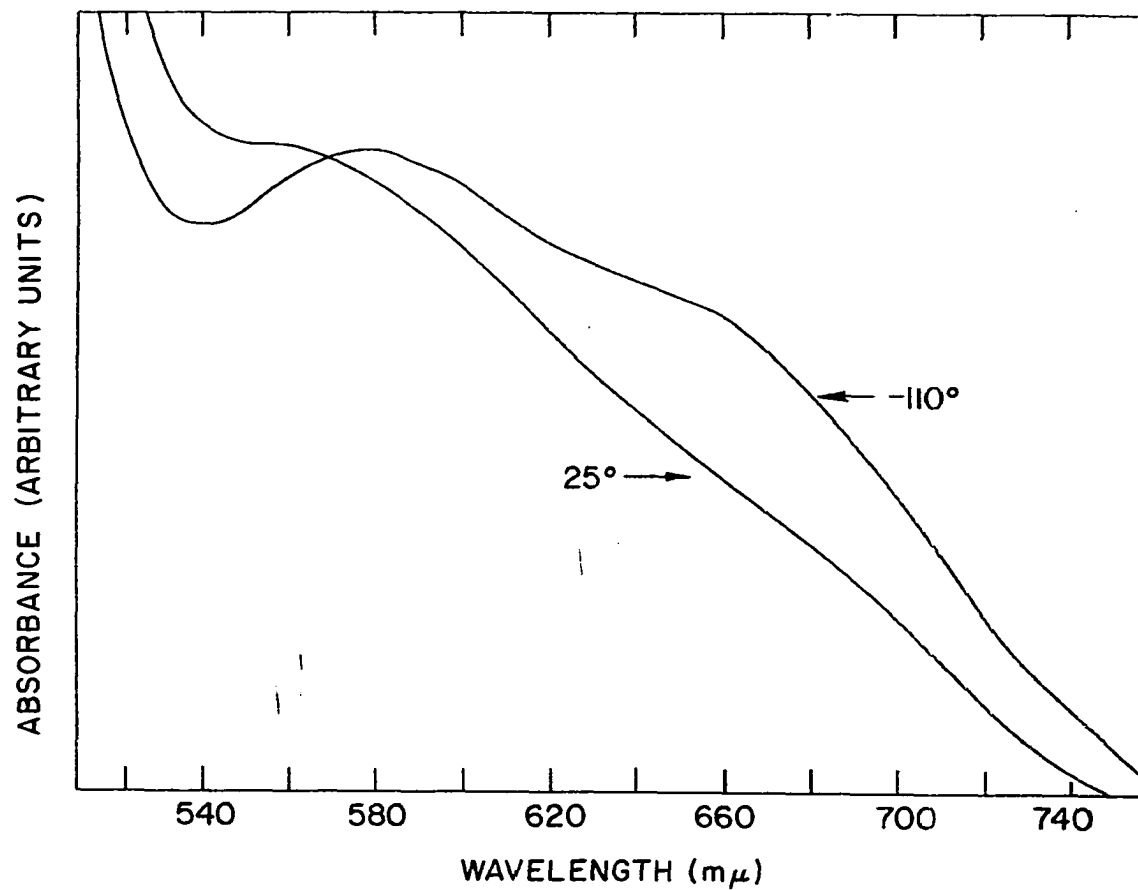


Figure 1. Temperature dependence of visible spectrum of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$ in EtOH saturated with HCl

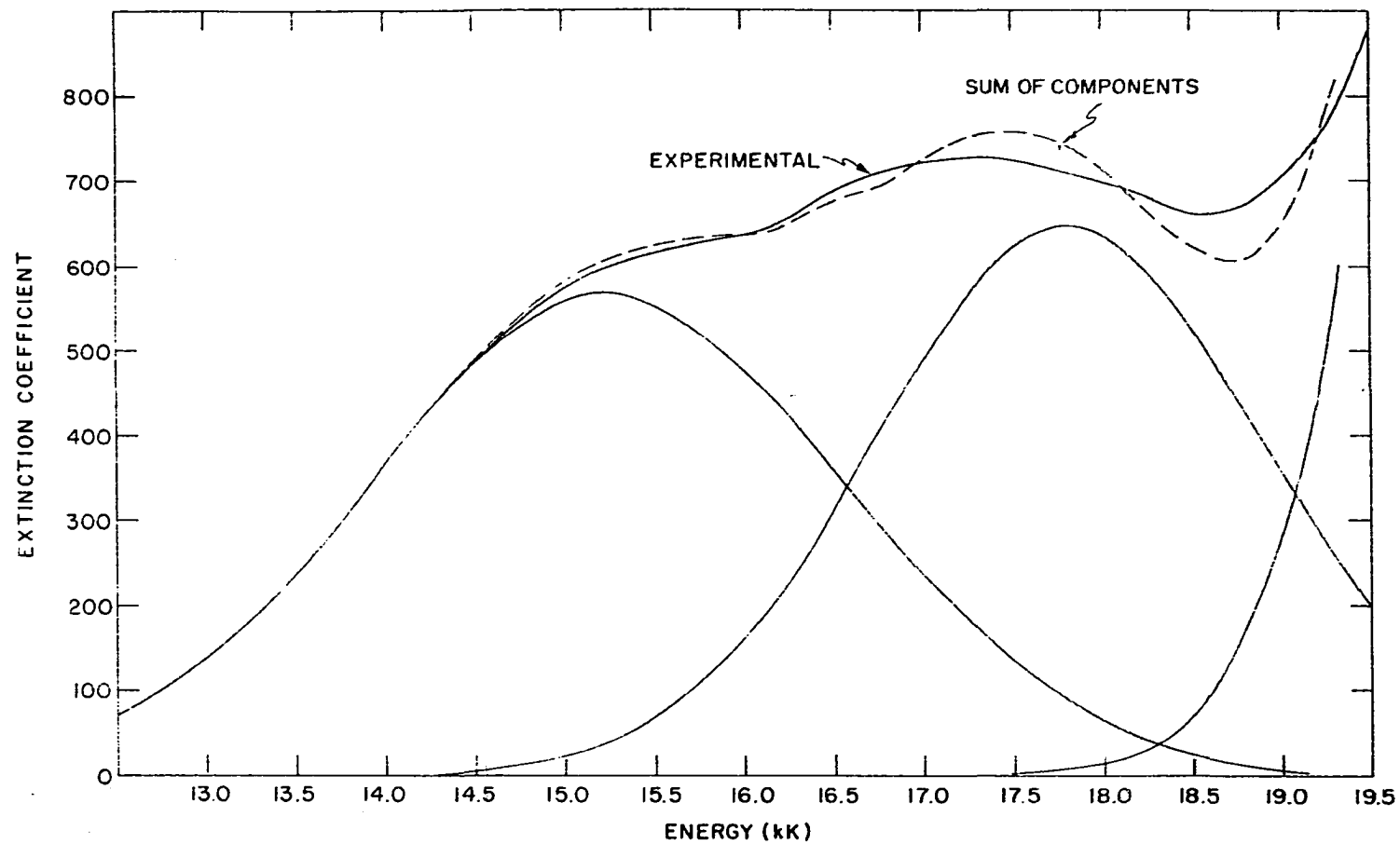


Figure 2. Visible spectrum of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$ in EtOH saturated with HCl at ca. -110°

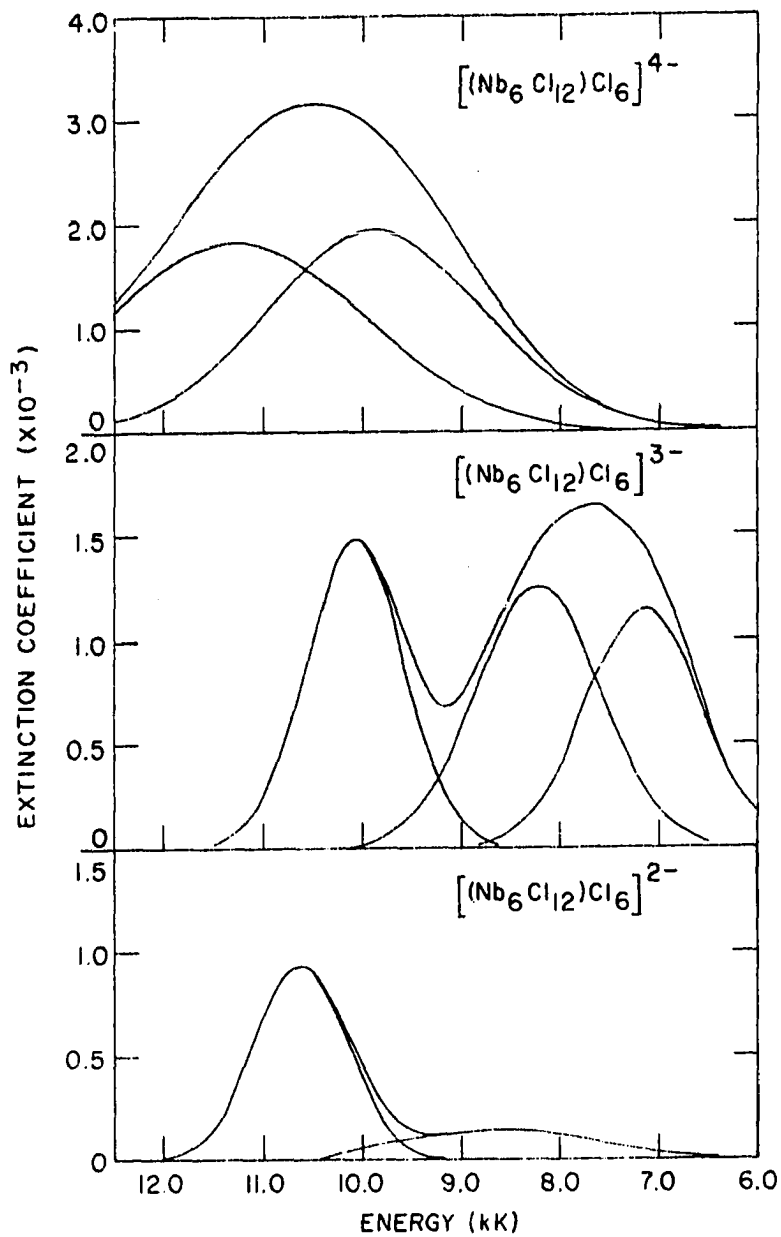


Figure 3. Near infrared spectra of niobium clusters in acetone

three oxidation states the behavior of the cluster in various solvents was studied. Previous work by Mackay (17) on the conductance of $(\text{Et}_4\text{N})_n[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ ($n = 2,3,4$) in nitromethane has shown that the cluster complexes are $n:1$ electrolytes. The conclusion drawn from these data is that the terminal chlorides are not appreciably dissociated. Far infrared data obtained by Mackay (17) on $(\text{Et}_4\text{N})_n[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ complexes in nitromethane agree within a few cm^{-1} of data on the solids and may be used to support the contention that the terminal chlorides remain associated with the cluster.

It was thought that if optical spectra for various cluster anions in different solvents including nitromethane could be compared, a judgement on the species present could be made. Using the data from different solvents given in Table 1 such a comparison can be made. Only the major absorption maxima are reported in the table, and as will be discussed later, some of the maxima in the near infrared actually consist of two slightly separated bands.

The nitromethane solutions were measured only for the 3+ and 4+ cluster complexes, but Mackay's data (17, p. 103) could not be duplicated for the 4+ compound because an apparent reaction of the cluster with the solvent occurred. How-

Table 1. Major absorption maxima (m μ) for some Nb₆Cl₁₂ⁿ⁺ species

Compound ^a	Solvent							
	H ₂ O	C ₂ H ₅ OH	DMSO	C ₂ H ₅ OH ^b + HCl(g)	CH ₃ CN	CH ₃ NO ₂ ^c	Acetone	Solid reflec- tance
R ₄ [(Nb ₆ Cl ₁₂)Cl ₆]	397		413 931	415 955	412 932	440 1010 1315	418 967	418 970
[Nb ₆ Cl ₁₂]Cl ₂ ·8H ₂ O	395 895	405 ^d 425	412 931				410 936	402 910
R ₃ [(Nb ₆ Cl ₁₂)Cl ₆]		434 968 1255	442	438 990	440 1010 1310	442 1010 1308	442 1011 1303	440 1005
R ₂ [(Nb ₆ Cl ₁₂)Cl ₆]		455 943	442	457 940	458 941	456 935	460 950	465 959

^aR is Li⁺ and K⁺ (reflectance only) for 2+; R is n-prNH₃⁺ and Et₄N⁺ (reflectance only) for 3+ and 4+.

^bEthanol saturated with hydrogen chloride; solutions prepared as in experimental section.

^c2+ and 4+ data according to Mackay (17, p. 103) on Et₄N⁺ complexes (see text for discussion).

^dData taken from Mackay (17, p. 98) and Robin and Kuebler (7).

ever, maxima at 458 and 941 $m\mu$ were obtained for $(n\text{-prNH}_3)_2$ $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ in nitroethane. Because these latter data and those for the 3+ cluster agree fairly well with the maxima obtained on the solid state no appreciable solvolysis was indicated. A comment on the data reported by Mackay (17, p. 98) for the 2+ cluster is in order at this point. On comparison of these data with those obtained for the 3+ and 2+ clusters in this work it appears that Mackay was actually dealing with a 3+ cluster.

Further comparison of the data in Table 1 allows the following conclusions regarding the cluster species present. Because spectra on acetone solutions of the cluster complexes agree closely with the solid state spectra, the anionic species, $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$, can be presumed to be present. Other solvents where the displacement of terminal chloride is slow are acetonitrile and DMSO, and also it is seen that the cluster is nearly completely anated in ethanol saturated with hydrogen chloride. The data indicate that ease of anation of the cluster follows the order $4+ > 3+ > 2+$. This order is reasonable from qualitative charge considerations since the fully anated cluster anions would have the charges 2-, 3-, and 4-, respectively. The strong tendency for the 2+ cluster

to be oxidized by oxygen in the presence of high chloride concentration is indicative of the stabilization of higher oxidation states by anation.

Information on the effect of varying the terminal ligand on the clusters can be obtained in a general way from the data in Table 1. Note that in the case of the 2+ cluster where it is evident that at least four terminal ligands are different than chloride, corresponding bands are shifted to higher energies (lower wavelength). Thus, it can be stated that oxygen donors have a greater hypsochromic effect than chloride which is in accord with the well known spectrochemical series (37, p. 109). Field and Kepert (19) have reported a more extended spectrochemical series for oxygen donor ligands bonded to the 2+ cluster. The details of their ordering may be open to question since some of their compounds appear to be 3+ rather than 2+. This latter conclusion stems from the fact that, for example in the near infrared, the lowest energy band observed in this study is at 10.3 kK for the 2+ cluster and many of the compounds reported by Field and Kepert have a band at an energy less than 10.3 kK.

The behavior of the cluster in DMSO was found to be

unusual¹ and also useful for obtaining some spectra. The 4+ niobium cluster is reduced to the 3+ cluster in DMSO at 25° with no appreciable displacement of terminal chlorides as determined by examining the visible spectrum. This reaction was utilized to obtain a spectrum of the anion $[(\text{Nb}_6\text{Br}_{12})\text{Br}_6]^{3-}$ since the corresponding solid complex was not synthesized. In other studies it was observed that the 4+ tantalum cluster can be reduced fairly rapidly to the 3+ in DMSO with gentle warming, and to the 2+ state with more vigorous warming (~70°) for a few hours. The niobium clusters appear to be reduced more readily than the corresponding tantalum clusters.

Another aspect of the chemistry of the niobium clusters which was noticed in this study was their apparent degradation, especially of the 3+ and 4+, in acetone. Acetone solutions yield white precipitates after standing at 25° for more than a few days. The precipitate which was presumed to be Nb_2O_5 may be formed via an oxygen abstraction reaction with the solvent as has been shown to occur between molybdenum(V) chloride and some oxygen donors (38), or tungsten(VI) chloride

¹Grindstaff, W. K. Ames, Iowa. Reactions of niobium halide clusters with DMSO. Private communication. 1967.

and acetone (39). However, decomposition of the cluster, and in fact, the above reported oxygen abstraction reactions could occur because of the presence of water in the reaction system.

Electronic spectra data

The electronic spectra obtained for a series of cluster ions which are generally of the type $[(M_6X_{12})Y_6]^{n-}$, as discussed previously, are reported in tabular form in Tables 2-6. The data are reported in kK (1000 cm^{-1}) for energy, molar extinction coefficient ($\ell \text{ mole}^{-1} \text{ cm}^{-1}$) for intensity, and kK for the band half-width at half height. The extinction coefficients were obtained from room temperature data, whereas the band maxima positions and half-widths were obtained from both low temperature and room temperature measurements.

It has been observed in this work that δ , the half-width, is decreased by approximately 10-12% on lowering the temperature from ca. 300° to 200° K . These changes in half-width with temperature have not appeared to be significant as regards correlating bands in different cluster spectra, especially when an approximate factor is used to normalize δ to room temperature.

Band positions can also be compared without regarding

the temperature effect which has been found to raise the energy by only about 100 cm^{-1} . This value amounts to about one per cent of the energy of the bands in the near infrared; it is less elsewhere and is not significant in this work. In other transition metal complexes the shift of absorption bands to higher energies at lower temperatures is a well known effect. It has been attributed partially to the quenching of ground state vibrations, and to an increase in the effective ligand field on cooling (37, p. 145, 40).

The experimental spectra will be discussed in this section along with data obtained by other workers. Then a consideration of the implications in regards to the cluster electronic structure will be made.

The data in Tables 2-6 are presented so that corresponding bands for different species and oxidation states lie in the same rows. The spectra are most conveniently discussed in three separate sections; the near infrared, visible, and ultraviolet.

In Table 2 data for the three oxidation states of the niobium chloride cluster in the anions $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$ are summarized. The 4+ spectrum has the relatively obvious major bands resolved in the visible and near infrared (see Figure

Table 2. Absorption maxima for $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$ species^a

$[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$			$[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{3-}$			$[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$		
$\nu(\text{kK})$	$\epsilon \times 10^{-3}$	$\delta(\text{kK})$	$\nu(\text{kK})$	$\epsilon \times 10^{-3}$	$\delta(\text{kK})$	$\nu(\text{kK})$	$\epsilon \times 10^{-3}$	$\delta(\text{kK})$
10.02	1.83	.98	7.16	1.14	.69	-----	-----	-----
11.27	2.09	1.24	8.23	1.26	.74	-----	-----	-----
-----	-----	-----	-----	-----	-----	8.65	.15	1.15
-----	-----	-----	9.93	1.51	.58	10.57	.94	.53
16.8	.57	2.2	15.5	.27	1.4	15.2	.56	1.6
20.3	1.10	1.4	18.6	.69	1.5	17.8	.65	1.3
23.9	10.27	1.5	22.8	7.35	1.3	21.9	13.56	1.1
30.1	3.1	2.4	28.1	1.8	3.2	27.4	3.9	3.2
35.5	10.3	2.1	35.1	20.	2.8	33.3	26.5	2.3
-----	-----	-----	-----	-----	-----	39.	20.	-----
42.7	27.	2.6	43.0	79.	3.3	42.7	84.	2.8
46.8	48.	2.2	46.2	43.	2.0	46.4	15.	1.1
-----	-----	-----	-----	-----	-----	50.4	91.	4.7

^aMaxima are resolved Gaussian components. Spectra obtained on ethanol + HCl solutions containing $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$, or acetone or acetonitrile solutions of $(n\text{-prNH}_3)_n[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$.

3). The ultraviolet region of the spectrum (greater than 30 kK) is not as clear cut because of the large number of high intensity bands in that region. The four bands other than that located at 39 kK are certainly real and their positions are established. The three lowest energy bands excepting that at 39 kK also are present in the 2+ and 3+ spectra, but the 50.4 kK band found in the 4+ spectrum is unique. Its position would be at even higher energy in the lower oxidation states, and thus out of the range of the spectrophotometer.

The weak band at 8.65 kK which has not been reported before, actually is the least intense band found for any of the niobium clusters. The questionable band at 39 kK also has not been previously reported. Mackay (17, p. 97ff) has reported approximate positions for all of the remaining bands although these positions differ from the present ones by up to 800 cm^{-1} for the weaker bands and also the species measured is not as clearly defined.

The number of bands for the 2+ and 3+ hexachloro anions is not as easy to establish as for the 4+. The visible and ultraviolet regions are relatively straightforward and certainly exhibit the number of bands reported. The near infrared region (Figure 3) exhibits two absorption ranges for the

3+, the higher energy of which is certainly the one narrow band located at 9.93 kK. There is also a broad absorption region at lower energy which is not obviously any more than one band, and in the 2+ there is one strong and fairly symmetrical absorption centered at ca. 10.5 kK.

In the case of the 3+ cluster the problem can be resolved by considering the resolution of the broad absorption centered at ca. 7.8 kK into Gaussian components. If an attempt is made to treat this absorption as one band it is found that a satisfactory Gaussian fit cannot be realized. The absorption is too broad at the maximum and too narrow in the region where $\epsilon < \epsilon_{\max}/2$. However, the absorption can be resolved very satisfactorily into two Gaussian components which, as seen in Table 2, have reasonable band parameters, especially the half-width.

In the 2+ spectrum, the near infrared absorption can be fitted reasonably well by one Gaussian with a $\delta (+)$ of 1.8 kK and a $\delta (-)$ of 1.5 kK for 25⁰ data in acetone. Note that here the convention of Jørgensen (31) is used where two different half-widths can be used in forming Gaussian spectral components and $\delta (-)$ and $\delta (+)$ refer to the regions where $\nu < \nu_0$ and $\nu > \nu_0$ respectively. As an example it is noted that Jørgen-

sen (31) has used Gaussian error curves with δ (+) up to 40% greater than δ (-) although generally the difference is 0-10%. This absorption can also be fitted with two Gaussian error curves as indicated in Table 2 and Figure 3, although at 25° the half-widths are 1290 and 1510 cm^{-1} for the low and high energy bands respectively. The half-widths found for either one band or two bands are within the range of expected values. The resolution of the spectrum obtained either at 25° or -110° (ethanol slush) was not definitive and either of the above alternatives was possible.

In an additional attempt to solve this problem the spectrum of a glycerol glass of $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ was obtained. It was hoped that the combination of the non-symmetric terminal ligand field around the cluster (by analogy to $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (21)) and low temperature (the glass was maintained at -196° for 12 hrs. prior to running the spectrum) would indicate the presence of two bands in the near infrared spectrum. A sharp spectrum was obtained, but no shoulders were found on the band in question.

The reasons for assigning two bands to the near infrared spectrum of the 2+ niobium cluster evolve to the following:

1) the absorption can be fitted with two bands. 2) it is

reasonable to expect that the 2+ cluster should have two bands corresponding to the two found at 7.16 and 8.23 kK in the 3+ (this will be elaborated on when the electronic structure is discussed). 3) it is reasonable to expect the tantalum and niobium clusters to have the same number of bands (Table 6).

Some comments on 2+ and 3+ niobium cluster spectra obtained by other workers is in order at this point. Allen and Sheldon (6) have reported the spectra of $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ in neutral and basic solution. The spectrum reported in water agrees with that found in these studies although as noted earlier (9) the extinction coefficients obtained here are 15-50% higher.

Robin and Kuebler (7) have reported the spectra of $\text{Nb}_6\text{X}_{12}^{2+}$ (X = Cl, Br) in ethanol which are similar to the spectra found in this study. However, they assign only one band in the near infrared region and also do not report a band at 42.7 in the ultraviolet.

Mackay (17, p. 97ff) has examined the spectra of the 2+ and 3+ complexes, $[\text{Et}_4\text{N}]_n[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$, in ethanol and nitromethane. In ethanol the spectrum of the 2+ cluster has a 1:1 correspondence with that obtained here but band positions are shifted ca. 800 cm^{-1} to higher energy. This effect is prob-

ably due to displacement of terminal chloride by ethanol, e.g., the prominent band in the visible is at 24.7 kK compared to 23.9 kK for $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$ and 24.7 kK for $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}]$ in ethanol. Mackay's data for the 3+ cluster in ethanol do not include the low energy bands at 7.16 and 8.23 kK, or the weaker bands at 15.5 and 28.1 which are stated to be present but are not located explicitly.

The prominent bands reported by Mackay, 10.4, 18.2, 23.5, 34.7, 43.5, and 45.9 kK, are shifted to higher energy by $5-700 \text{ cm}^{-1}$, as was found in the 2+ case. The reason for this is presumed to be the same as for the 2+, i.e., displacement of terminal chloride by solvent molecules.

In nitromethane the data of Mackay (17) indicate that both the reported 2+ and 3+ spectra are actually 3+. For the 3+, bands reported at 7.6, 9.9, 14.6, 18.0, and 22.7 kK are in substantial agreement with those found in this study. In nitromethane, as pointed out previously, the species present is the hexachloro anion.

The major disagreement with earlier work, then, is in the near infrared region of the spectrum. Mackay did assign two bands to the 2+ spectrum in this region although partial justification for this assignment was the spectrum in nitro-

methane which showed two bands and was incorrectly attributed to the 2+ cluster. The correlation of the 3+ band at 9.93 kK with the 4+ band at 10.57 kK is indicated by the small energy difference, similar half-width, and comparable extinction coefficient. These bands do not appear to have a counterpart in the 2+ spectrum. Instead, the broad absorption in the 7-8 kK range in the 3+, which Mackay assigned as one band at 7.6 kK, correlates nicely with the broad 2+ absorption. Each band system is then resolved into two components with similar parameters, ν_0 , ϵ_0 , and δ , which also appear reasonable on the grounds that transitions of the same type should give rise to similar band parameters within a given cluster sequence.

The region from 4 to 7 kK deserves some comment. Preliminary work by J. Converse on the spectra of tantalum cluster compounds in acetone had indicated that a band at ca. 5.2 kK was present¹. The band appeared to be quite narrow and intense in the $\text{Ta}_6\text{X}_{12}^{4+}$ (X = Cl, Br) spectra in acetone. These spectra were obtained on a solution extracted from $\text{TaBr}_{2.83}$ (11,41) with acetone, $[\emptyset_4\text{As}]_2[(\text{Ta}_6\text{Br}_{12})\text{Br}_6]$, and $[\text{Et}_4\text{N}]_2[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]$ in acetone. This band was also observed

¹Converse, J. G. Ames, Iowa. Spectra of some tantalum cluster compounds in the near infrared. Private communication. 1967.

in 3+ spectra and possibly in 2+ spectra although the purity of the cluster is questionable in the latter case. In any event, the band was observed independently of cation, halogen, and as far as position is concerned, oxidation state of the cluster.

In view of the above observations this region of the spectrum was investigated for all oxidation states of the niobium cluster in several solvents and in potassium chloride wafers. The results of the solution studies showed a very weak absorption at 5.25 μ K in the 4+ spectra and an intense absorption at 5.25 μ K in the 3+ spectra. The band position was effectively invariant for the 3+ hexachloro anion as either the Et_4N^+ or n-prNH_3^+ salt in acetone, acetonitrile, or nitromethane. The band parameters, ϵ_0 and δ , at 25 $^\circ$ in acetone were 890 $\text{l mole}^{-1}\text{cm}^{-1}$ and 45 cm^{-1} respectively. This band also had an apparent dependence on cluster concentration. However, it was not observed in the solid state wafer spectra whereas all of the other bands observed in the solution spectra are evident in the solid state. The origin of this apparent band is not evident, but in view of its absence in the solid state spectra, the extremely small half-width, and the fact that its position is the same for both the niobium

and tantalum clusters it is considered to be spurious. There were no bands noted in the 2+ niobium spectrum other than those recorded in Table 2.

In Table 3 the spectra of some 4+ clusters where the inner and terminal halogens have been varied is recorded. All of the bands described for the hexachloro 2- anion above are seen to be present when either the inner or terminal chloride ions are changed to bromide ions. The band parameters for corresponding bands are not significantly dependent on the halide ion. In the near infrared region the two bands for the hexabromo bromide cluster are seen to be somewhat more intense than those for the hexachloro chloride cluster. The possibility of some 3+ impurity being present in the complex $[\text{n-prNH}_3]_2[(\text{Nb}_6\text{Br}_{12})\text{Br}_6]$ which would lead to enhancement of the intensity of the spectrum in this region cannot be precluded. Magnetic susceptibility measurements which would give an indication of paramagnetic (3+ cluster) impurity have not been made on this compound.

On comparing the spectra of the 4+ chloride cluster anions it is seen that the prominent bands in the near infrared are shifted to slightly higher energies on substituting terminal bromide for chloride. The strong band in the visible

Table 3 . Absorption maxima of some $[(\text{Nb}_6\text{X}_{12})\text{Y}_6]^{2-}$ species

$[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$ ^{a,b}			$[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]^{2-}$ ^c			$[(\text{Nb}_6\text{Br}_{12})\text{Br}_6]^{2-}$ ^{a,c}		
$\nu(\text{kK})$	$\epsilon \times 10^{-3}$	$\delta (\text{kK})$	$\nu(\text{kK})$	$\epsilon \times 10^{-3}$	$\delta (\text{kK})$	$\nu(\text{kK})$	$\epsilon \times 10^{-3}$	$\delta (\text{kK})$
8.65	.15	1.15	9.00	.15	----	7.75	.40	1.20
10.57	.94	.53	10.79	1.00	.48	9.43	1.19	.57
15.2	.56	1.6	15.5	.51	----	14.0	.50	1.5
17.8	.65	1.3	17.9	.76	----	16.6	.97	1.3
21.9	13.56	1.1	21.6	15.2	1.3	20.5	14.49	1.3
27.4	3.9	3.2	28.2	wk	----	25.4	3.2	2.2
33.3	26.5	2.3	32.0	21.6	----	29.6	13.8	3.2
39.	20.	---	39.	30.	----	33.	----	---
42.7	84	2.8	41.2	75.	----	36.3	50.	2.5
46.4	15.	1.1	46.9	95.	----	41.1	85.	2.2
50.4	91.	4.7	----	----	----	47.9	126.	4.8

^aMaxima are resolved Gaussian components.

^bSpectra obtained on ethanol + HCl solutions containing $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$ or acetone solutions of $(\text{n-prNH}_3)_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$.

^cSpectra obtained on solutions of $(\text{n-prNH}_3)_2[(\text{Nb}_6\text{X}_{12})\text{Y}_6]$ in acetone or acetonitrile.

is shifted from 21.9 kK to 21.6 kK on changing terminal chloride to bromide. Shifts in the less prominent bands are not as meaningful when of this small magnitude due to the uncertainty in obtaining exact positions by the resolution technique used.

The effect of changing inner halide ions is much more drastic than changing terminal halides. Table 3 gives the details of the 4+ hexabromo bromide spectrum, and in Table 4 the 4+ and 3+ hexabromo and hexachloro bromide and chloride clusters, respectively, are compared. $\Delta \nu_{\max}$ represents the difference in energy between the bands. It is seen that in the visible and near infrared regions of the spectrum (<29 kK) the band energies decrease by 1-2 kK on going from the chloro to bromo cluster. The effect is even less in the two band system at lowest energy in the 3+ clusters.

All except one of the bands at higher energy than 29 kK exhibit shifts of from ca. 4-7 kK to lower energy on changing chloride to bromide. These bands are in the proper region for what are normally termed charge transfer bands and even though in the 4+ chloride cluster the 50.4 kK band only shifts to 47.9 kK in the bromide it should be included as a charge transfer because of its high energy and the uncertainty in measurements near the solvent cut off.

Table 4. Absorption maxima of $[(\text{Nb}_6\text{X}_{12})\text{X}_6]^{2,3-}$ (X=Cl,Br)

$[(\text{Nb}_6\text{X}_{12})\text{X}_6]^{2-}$			$[(\text{Nb}_6\text{X}_{12})\text{X}_6]^{3-}$		
X=Cl ^a ν_{max} (kK)	X=Br ^a ν_{max} (kK)	$\Delta\nu_{\text{max}}$ (Cl-Br)	X=Cl ^a ν_{max} (kK)	X=Br ^b ν_{max} (kK)	$\Delta\nu_{\text{max}}$ (Cl-Br)
			7.16	7.0	.16
			8.23	8.1	.13
8.65	7.75	.90			
10.57	9.43	1.14	9.93	9.01	.92
15.2	14.0	1.2	15.5	14.3	1.2
17.8	16.6	1.2	18.6	17.5	1.1
21.9	20.5	1.4	22.8	21.4	1.4
27.4	25.4	2.0	28.1	----- ^c	-----
33.3	29.6	3.7	35.1	31.0	4.1
39.	33.	6.	not observed		-----
42.7	36.3	6.4	43.0	35.8	7.2
46.4	41.1	5.3	46.2	39.4	6.8
50.4	47.9	2.5			

^aMaxima are resolved Gaussian components.

^bMaxima are estimated from recorder data; spectrum obtained in DMSO.

^cBand is present but too ill-defined to locate.

The reason for considering these ultraviolet bands as arising from inner halide to metal charge transfer is given below. In general, charge transfer bands of octahedral hexahalometallate complexes show a shift to lower energy of about 6-8 kK on going from chloride to bromide (37, p. 146ff). In fact, this generalization also holds true for the halide ions in aqueous solution or in alkali metal halide crystals, and thus appears to be nearly independent of the halogen environment. For example, the apparent charge transfer bands in the alkali metal complexes, M_2NbX_6 ($X = Cl, Br$), are at 9.2 to 9.7 kK lower energy for the bromo complex (42).

A question on the nature of the band in the 30-35 kK region of the spectra (Table 4) may arise because of the smaller energy shift. The shift is larger by about a factor of two than the band shifts found in the visible spectra and therefore appears to have a different origin. This band may involve a transition from an orbital which has less halogen character than the others giving rise to the ultraviolet spectrum.

Another point which is interesting to note is that there is not a significant energy shift in the ultraviolet bands when the oxidation state of a particular cluster is varied.

For example, the energy of the charge transfer bands of hexahalometallate complexes are at ca. 5 or more kK higher energy on changing the metal oxidation state from 4+ to 3+. The magnitude of the shift is dependent on the d^n configuration and type of charge transfer being considered (37). The reason for the small change in band position on changing the cluster oxidation state is probably partially due to the fact that a one unit change in oxidation state of the cluster amounts to only a 1/6 change per niobium atom.

In Table 5 and Figure 4 the spectra of the tantalum chloride cluster in its three oxidation states are reported. The 2+ and 3+ measurements were made on what were probably solvated cluster cations. The 3+ spectrum was obtained on $[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol and by analogy to work in the niobium system the spectrum would be shifted to higher energies than if the anion $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]^{3-}$ was present. The band positions for the 3+ cluster obtained here do agree quite closely with those obtained by Espensen and McCarley (15) for $\text{Ta}_6\text{Cl}_{12}^{3+}(\text{aq.})$. Thus, when comparing the 3+ spectra to others reported for hexahalo anions approximately 400-900 cm^{-1} should be subtracted from the 3+ band positions for the near infrared through visible regions, respectively. The 2+

Table 5. 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		
ν (kK)	$\epsilon \times 10^{-3}$	δ (kK)	ν (kK)	$\epsilon \times 10^{-3}$	δ (kK)	ν (kK)	$\epsilon \times 10^{-3}$	δ (kK)
						8.64	.05	.5
						10.1	.32	.5
12.7	2.2	1.1	10.6	1.5	.9	----	----	---
15.2	3.8	1.5	13.6	1.7	.9	----	----	---
----	---	---	12.1	2.0	.95	11.85	1.3	.8
20.4	1.2		----	---	---	19.2	1.0	1.4
25.0	6.		23.2	2.2		22.5	2.5	1.7
29.9	30.		29.0	14.5		27.1	26.5	1.2
34.5	8.		36.4	8.		35.1	8.4	1.9
42.2	20.		42.5	16.		40.3	18.5	2.7

^aData reported is estimated from the raw data and are not resolved bands. The compounds used to obtain these spectra were prepared by J. L. Meyer (18).

^bMeasured in DMSO as a solvated cation.

^cMeasured in EtOH as a solvated cation.

^dMeasured in acetone as the hexachloro anion.

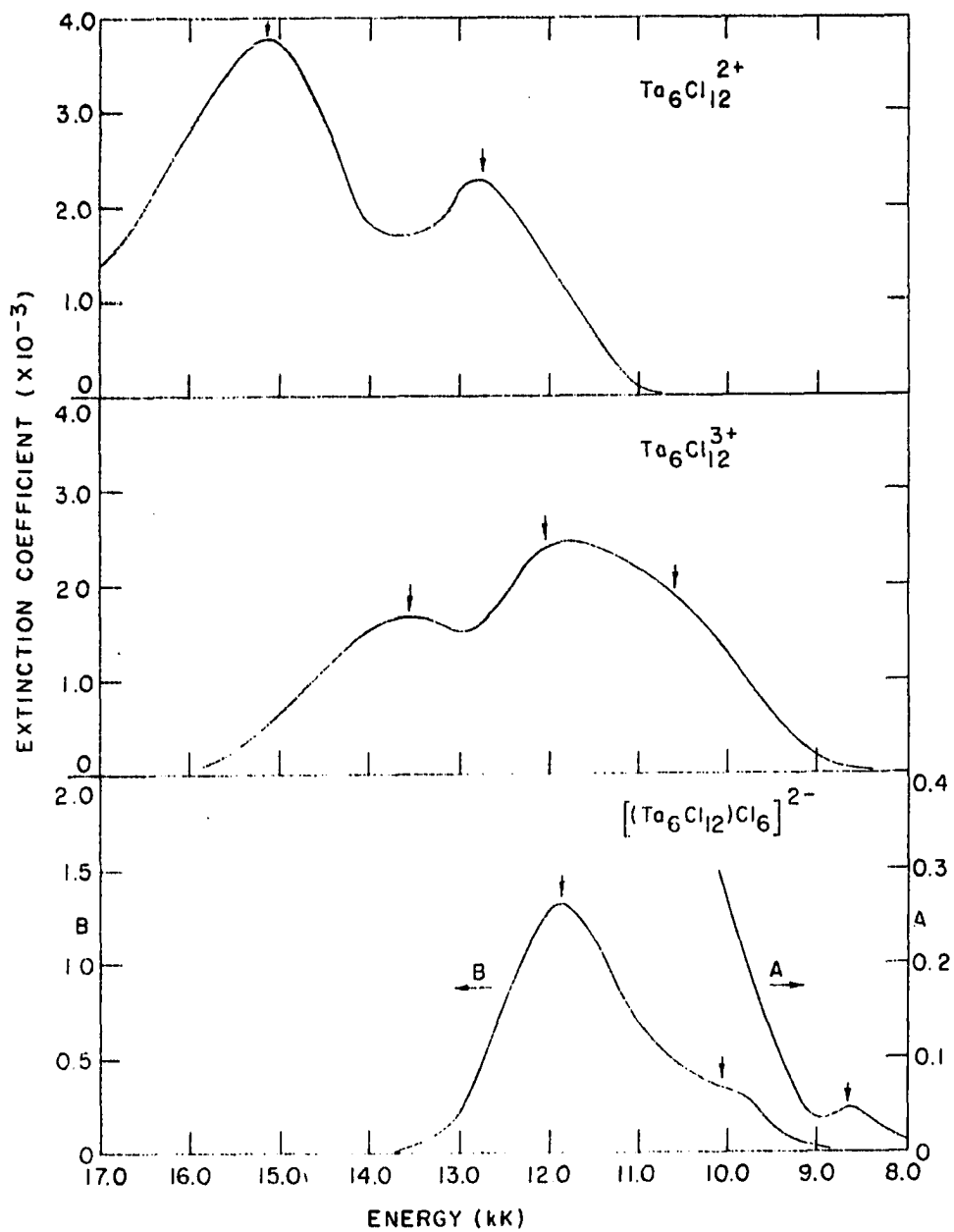


Figure 4. Near infrared spectra of tantalum clusters

spectrum was obtained in DMSO, which by analogy to the niobium system (Table 1) gives higher energies than the hexahalo anions by about $400-500 \text{ cm}^{-1}$.

The tantalum cluster spectra are seen to be qualitatively similar to the niobium spectra having the same relative band intensities and positions. In Table 6 it is seen that the tantalum band positions are from ca. 2-8 kK higher energy than those of the niobium spectra except for the two weak near infrared bands. This result is in general agreement with the 6-9 kK shift to higher energy found on comparing $4d^n$ to $5d^n$ hexahalo complexes (37, p. 154). For example, for the alkali metal complexes of the MCl_6^{2-} ($M = Nb, Ta$) anions in the ultraviolet charge transfer spectrum $\Delta\nu_{\max}(Ta-Nb)$ is 6-7 kK and in the visible ligand field spectrum $\Delta\nu_{\max}(Ta-Nb)$ is ca. 1 kK (42).

It is seen in Table 6 that the niobium and tantalum cluster spectra have been brought into a 1:1 correspondence. This correspondence in the visible is relatively obvious when the band parameters are considered, e.g., the $4+$ spectra all have four visible bands with ϵ_{\max} ratios of; Ta, 1:2.5:26:8; Nb, 1:1.2:24:7.

The correspondence in the near infrared region is less

Table 6. Comparison of absorption maxima (ν_{\max}) of $M_6Cl_{12}^{n+}$ (M=Nb,Ta) containing clusters

1 ^a	$\Delta\nu$	2 ^b	3 ^c	$\Delta\nu$	4 ^d	5 ^e	$\Delta\nu$	6 ^f
ν_{\max} (kK)	1-2	ν_{\max} (kK)	ν_{\max} (kK)	3-4	ν_{\max} (kK)	ν_{\max} (kK)	5-6	ν_{\max} (kK)
						8.64	---	----
						10.1	1.4	8.65
12.7	2.7	10.02	10.6	3.4	7.16	----	---	----
15.2	3.9	11.27	13.6	5.4	8.23	----	---	----
----	---	----	12.1	2.2	9.93	11.85	1.3	10.57
20.4	3.6	16.8	----	---	15.5	19.2	4.0	15.2
25.0	4.7	20.3	23.2	4.6	18.6	22.5	4.7	17.8
29.9	6.0	23.9	29.0	6.2	22.8	27.1	5.2	21.9
34.5	4.4	30.1	36.4	8.3	28.1	35.1	7.7	27.4
42.2	6.7	35.5	42.5	7.4	35.1	40.3	7.0	33.3

^aTa₆Cl₁₂²⁺.

^b[(Nb₆Cl₁₂)Cl₆]⁴⁻.

^cTa₆Cl₁₂³⁺.

^d[(Nb₆Cl₁₂)Cl₆]³⁻.

^e[(Ta₆Cl₁₂)Cl₆]²⁻.

^f[(Nb₆Cl₁₂)Cl₆]²⁻.

obvious. If, as discussed earlier, the niobium 2+ spectrum has two bands in the near infrared the 2+ niobium and tantalum spectra correspond. The 2+ tantalum bands are then assigned as arising from the same transitions as those 3+ bands at 10.6 and 13.6 kK. The 12.1 kK band is thought to correspond to the 11.85 kK band in the tantalum 4+ cluster because of the close band positions and the $\epsilon_{\max}(3+)/\epsilon_{\max}(4+)$ ratio of 1.5 which is close to that of 1.6 in the niobium spectra. With the above arguments used to bring the 2+ and 3+ niobium and tantalum spectra into correspondence only the two weakest 4+ bands remain to be considered.

The 10.1 kK band appears to have its analog at 8.65 kK in the niobium system whereas the very weak 8.64 kK band is extra. This band could very well be unobserved in the niobium 4+ spectrum because of its expected low extinction coefficient ($<50 \text{ l mole}^{-1}\text{cm}^{-1}$) and the possibility of it being "hidden" under the tail of the 8.65 kK band. It is assumed, then, that these two low energy 4+ bands are forbidden transitions which are slightly allowed via an undetermined mechanism.

The spectra obtained by Robin and Kuebler (7) deserve more than the cursory account given in the Introduction. It

was noted there and also by Mackay (17, p. 113) that the $\text{Ta}_6\text{Cl}_{12}^{4+}$ spectrum is actually that of $\text{Ta}_6\text{Cl}_{12}^{3+}$. Robin and Kuebler had argued from their data that a distortion of the tantalum cluster occurred, resulting in a splitting of some of the bands. In addition to the apparent 1:1 correspondence of the tantalum and niobium spectra concluded above and by Mackay (17), new preliminary structural work indicates that the niobium and tantalum hexahalo cluster complexes have regular octahedra of metal atoms. The solid complexes, $\text{K}_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{1}$ and $\text{H}_2[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6] \cdot 8\text{H}_2\text{O}^{2}$, have been examined by single crystal techniques. It is reasonable to suppose that if these complexes were retained as the hexahalo anion 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 consequence in the spectra.

¹Schäfer, H. Münster, Germany. Single crystal x-ray studies on $\text{K}_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$. Private communication to R. E. McCarley. 1968.

²Jacobson, R. A. Ames, Iowa. Single crystal x-ray studies on $\text{H}_2[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6] \cdot 8\text{H}_2\text{O}$. Private communication to R. E. McCarley. 1968.

Electronic structure proposals

Several proposals for the bonding in the M_6X_{12} clusters have recently been made. These will be surveyed in more detail in this section along with their possible use as interpretive aids to the spectra.

In the molecular orbital treatment for M_6X_{12} clusters proposed by Cotton and Haas (27) the following method was applied. The metal atoms were assumed to use the d_{z^2} , d_{xy} , d_{xz} , and d_{yz} atomic orbitals to form metal-metal bonds. The $d_{x^2-y^2}$, s , and three p orbitals were not included in metal-metal bonding but were assumed to be used only for metal-halogen bonding. Note that this is tantamount to hybridizing s , p_x , p_y , and $d_{x^2-y^2}$ to bond the approximately square planar array of MX_4 atoms on each face of the M_6X_{12} cluster. Also, the p_z and d_{z^2} orbitals were not hybridized, and the interactions of the halogen p_π orbitals with the d -orbitals were neglected.

After choosing local coordinate systems on the metal atoms where each z axis points toward the octahedron center the symmetry representations which the d -orbitals span were determined. Symmetry orbitals were then constructed for the irreducible representations found above and energy expres-

sions found in terms of standard overlaps.

At this point, then, the overlaps needed to construct an orbital diagram were either computed or obtained from tables and results were plotted in terms of VSIP (unspecified) versus p . The parameter p is the product of the Slater orbital exponent, α , and the intermetallic distance in the cluster, R . The results of this study are shown in Figure 5.

There are several points to be noted about this molecular orbital ordering (27). First, configuration interaction of $t_{2g}(xz,yz)$ and $t_{2g}(xy)$ has not been included as a result of the zero overlap between the respective atomic orbitals. This interaction would tend to stabilize the $t_{2g}(xz,yz)$ and destabilize the $t_{2g}(xy)$. Second, if hybridization of the metal nd_{z^2} and $(n+1)p_z$ orbitals was allowed, the bonding $a_{1g}(d_{z^2})$ orbital would probably be stabilized and the antibonding molecular orbitals arising from d_{z^2} destabilized. Hybridization would not directly affect the other metal d -orbitals.

Cotton and Haas (27) made no attempt to rationalize physical data with their orbital ordering. However, Allen and Sheldon (6) assigned p values and attempted to rationalize their optical spectra. In using two p values (a unique

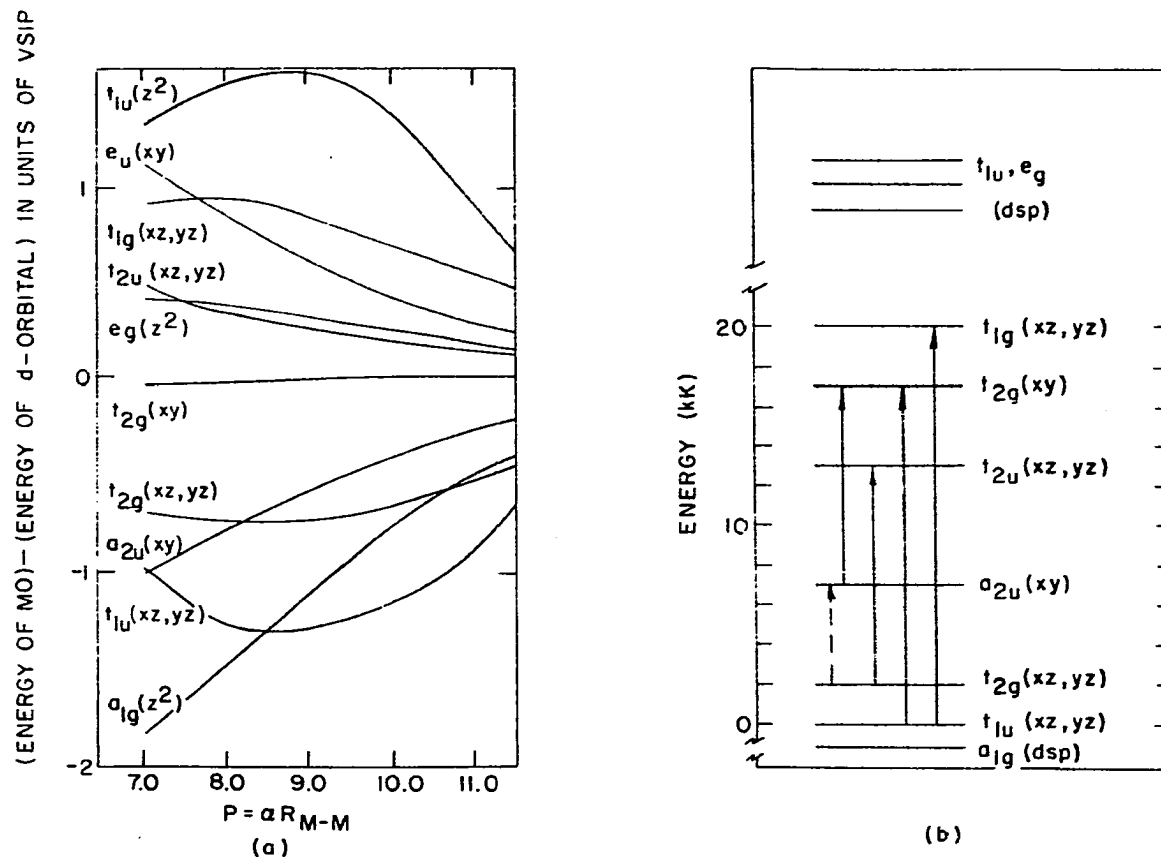


Figure 5. Proposed molecular orbital orderings for M_6X_{12} clusters
 (a) Result of calculations by Cotton and Haas (27)
 (b) Semi-empirical molecular orbital ordering by Mackay (17, p. 128) showing electronic transition assignments

value for the d_{z^2} orbitals) and an arbitrary VSIE, an orbital ordering allowing assignment of all of their eight bands (11.2, 16.5, 21, 25.2, 31, 36.5, 43, and 48.2 kK) for $\text{Nb}_6\text{Cl}_{12}^{2+}(\text{aq})$ to metal-metal transitions was arrived at. The ground state configuration was unclear from their work but would definitely not have the a_{2u} orbital as the top filled one because of the p values used.

Robin and Kuebler (7) extended the treatment of Cotton and Haas (27) and arrived at a rather different molecular orbital ordering. Since, as pointed out earlier, part of Robin and Kuebler's experimental data was treated incorrectly and their molecular orbital scheme drew heavily on these data, only the more important results are discussed here.

Robin and Keubler (7) proceeded by including all metal d -orbitals and inner ligand s and p -orbitals for $\text{Nb}_6\text{Cl}_{12}^{2+}$. Overlap calculations were made similarly to those of Cotton and Haas (27) only with the chloride atomic orbitals included. The general result was a raising of the various d -orbital manifolds because of metal-halogen overlap and a splitting of the manifold because of metal-metal overlap. The interesting result obtained was that the various d -orbitals separated into subsystems which were not mixed because of

local atomic orbital symmetry. Note that there is the possibility of mixing the m.o. subsystems when the mixing of ligand orbitals with the metal orbitals is taken into account. This effect was said to be negligible (7) and thus, was ignored.

The ground state configuration obtained by Robin and Kuebler (7) was $t_{1u}(xz,yz)^6 t_{2g}(xz,yz)^6 e_u(xy)^4$ which is drastically different from that due to Cotton and Haas (27), who found the e_u orbitals to be antibonding.

Several points concerning the assignment of spectral transitions by Robin and Kuebler (7) are worth considering. The spectra reported for niobium 2+ chloride and bromide clusters in ethanol appear good and essentially in agreement with those obtained here on similar solutions. For the major bands, ca. 11^1 , 16, 24, and 36 kK, Robin and Kuebler (7) report $\nu_{\max}(\text{Cl}) - \nu_{\max}(\text{Br})$ as 230, 1400, 1330, and 440 cm^{-1} and this difference is found as 200, 1100, 1600, and 800 cm^{-1} here. Note that the differences above are unusually and inexplicably small in relation to data reported for the hexahalo cluster complexes in the previous section. Robin and Kuebler (7) argue that a band shift of a few hundred cm^{-1}

¹Reported as one band, although believed to be two as discussed previously.

indicates a metal to metal transition whereas a shift of about 1 kK or greater is indicative of a ligand to metal charge transfer transition. The assignments finally arrived at by Robin and Kuebler are listed in Table 7.

Table 7. Transition assignments of Robin and Keubler (7)

$\text{Nb}_6\text{Cl}_{12}^{2+}$	
ν_{max} (kK)	Assignment
10	$e_u(xy) \rightarrow t_{2g}(xy)^a$
16.67	nb. ligand $\rightarrow a_{1g}(z^2)^b$
20.41	nb. ligand $\rightarrow a_{1g}(z^2)^b$
24.69	$\pi(t_{2g})$ ligand $\rightarrow a_{2u}(xy)^b$
31.25	forbidden ligand \rightarrow metal ^b
35.65	$t_{2g}(xz,yz) \rightarrow t_{2u}(xz,yz)^a$
46.39	(t_{2u}) ligand $\rightarrow a_{2g}(x^2-y^2)^b$

^aMetal to metal transitions.

^bLigand to metal charge transfer transitions.

These assignments were made on the basis that only fully allowed metal to metal transitions would appear in the spectra. A major factor in considering this band assignment scheme was that transitions between the various d-orbital subsystems were non-allowed, at least to the extent that they

would not be observed in the rich cluster spectra. This result is obtained because of the orthogonality of the metal d-orbitals and is without regard to the molecular orbital symmetry.

Mackay (17, p. 115ff) has proposed an alternative molecular orbital ordering, the gross features of which agree with Cotton and Haas (27). In this case the symmetry representations generated by the metal $(n-1)d$, ns , and np orbitals and the halogen (inner and terminal) ns and np orbitals were determined. Symmetry orbitals for the various equivalent atoms were formed and then combined to form molecular orbitals for the $[(M_6X_{12})Y_6]^{n-}$ cluster. The formation of the final molecular orbitals, which were not explicitly described, was not based on new calculation but rather on data previously published (7,27) and qualitative estimations of overlap.

The ordering of what were considered to be primarily metal-metal molecular orbitals is reproduced in Figure 5. The ground state configuration in this scheme is identical to that obtained by Cotton and Haas (27). There are differences in the antibonding orbitals with the $t_{2g}(xy)$ raised above the $t_{2u}(xz,yz)$. The t_{1u} and e_g orbitals arising from

the s, p, and d_{z^2} metal atomic orbitals were placed at highest energy which is a result of the hybridization. The $e_u(xy)$ orbital was not included in the metal-metal orbital scheme but was combined with the inner halogen $p_x p_y$ e_u orbitals and assigned as an antibonding metal-halogen m.o.

Mackay (17) has assigned the electronic spectra he obtained on the basis of the above orbital ordering. Possible transitions were considered on the basis of being symmetry allowed but the orthogonality of the various d-orbitals was not taken into account explicitly. Bands were assigned as shown in Table 8.

Examination of these assignments (17) led to a suggestion that metal-metal bands should have extinction coefficients of a relatively constant magnitude as ligand field bands of a given type do. A posteriori considerations led to the proposed criteria that metal to metal transitions within a given d-orbital subsystem should have extinction coefficients of 1000-3000 $\text{l mole}^{-1}\text{cm}^{-1}$ and transitions between different d-orbital subsystems, e.g., $\Gamma(d_{xy}) \rightarrow \Gamma(d_{z^2})$, should have extinction coefficients of less than 2000 $\text{l mole}^{-1}\text{cm}^{-1}$.

The intense absorptions in the spectra were then assigned as charge transfer bands (Table 8) of an unspecified type

Table 8. Transition assignments of Mackay (17)

$\text{Nb}_6\text{Cl}_{12}^{n+}$ ν_{max} (kK)	Assignment
5 (weak) ^a	$t_{2g}(xz,yz) \rightarrow a_{2u}(xy)^b$
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)	$a_{1g}, t_{2g}, \text{ or } t_{1u} \rightarrow t_{1u} \text{ or } e_g^c$
35 (16)	--- ^d
44 (39)	--- ^d
47 (83)	--- ^d

^aApproximate $\epsilon_{\text{max}} \times 10^{-3}$ listed in parentheses.

^bThis near infrared band was discussed earlier and considered spurious. Note that it should be present only for the 3+ and 4+ clusters.

^cMetal to metal transitions.

^dAssigned generally as either ligand to metal or metal to ligand charge transfer bands.

mainly because of their high extinction coefficients.

Prior to considering an assignment of the spectra obtained in this work it is appropriate to discuss in general terms the electronic structure of the cluster and the use of spectral selection rules.

Work in this laboratory by Converse (11) and elsewhere by others (7,8,17) has established via magnetic susceptibility measurements that the 2+ and 4+ clusters are diamagnetic and the 3+ cluster is paramagnetic (one unpaired spin). Also, esr data (8) have indicated that the 3+ unpaired electron is symmetrically delocalized over the M_6 octahedron in $[(Nb_6Cl_{12})Cl_6]^{3-}$ clusters. This evidence coupled with overlap considerations which suggest a strongly bonding, primarily metal a_{1g} (z^2) molecular orbital leads to the conclusion that the highest filled (2+) bonding m.o. is the $a_{2u}(xy)$.

The remaining bonding metal molecular orbitals can be obtained from the work of Cotton and Haas (27) although the exact ordering may be subject to discussion.

A point which has not been considered in previous studies on the electronic structure of the clusters is interelectronic repulsion and transitions between electronic states rather than configurations. In a cluster system where the electrons

are delocalized to a large extent interelectronic repulsion may be relatively low. However, electronic states arising from an excited configuration would not have to be separated by a large energy to account for the differences in band positions. No attempt to account for electronic states was made in this study but their presence should be borne in mind.

There are several selection rules which are pertinent to this discussion. The spin selection rule, $\Delta S = 0$, allows transitions between electronic states only when there is no change in total spin. Only spin allowed transitions which are also at least partially allowed via another mechanism are considered here. This arises because, generally, spin forbidden Laporte forbidden transitions have ϵ of ~ 0.1 and spin allowed, Laporte forbidden transitions have ϵ of 10-100 (43). For example, in the PtCl_4^{2-} system three spin forbidden bands have $\epsilon < 10$ and three spin allowed bands have $28 < \epsilon < 55$ (44,45).

The symmetry selection rule operates in several ways. In order to have a symmetry allowed transition the direct product $\Gamma_0 \Gamma_u \Gamma_n$, where Γ_0 is the ground state representation, Γ_u is the electric dipole moment operator representation, and Γ_n is the excited state representation, must

contain A_{1g} in O_h symmetry. Γ_u transforms as T_{1u} in O_h . In O_h a special case of the symmetry selection rule is also operative. This is the Laporte rule which states that only transitions between states of opposite parity are allowed (37, p. 102).

The above selection rules do not in general strictly hold true. There are two main factors which cause the relaxation of these rules and allow relatively weak transitions to be observed (43, p. 205ff). If vibrational excitation is considered in a molecule then some intensity can be induced for a Laporte forbidden transition by removal of the center of symmetry in the molecule and consequent mixing of some odd function, for example via a vibration of odd representation into an excited state of even representation. This allows a transition of partial $u \rightarrow g$ or $g \rightarrow u$ character. In a likewise manner the pure d character of a molecular orbital could be altered by mixing in some p character from a higher energy metal orbital or by mixing in some ligand p orbital contribution thus partially allowing an electronic transition. For example, extinction coefficients of ligand field bands in tetrahedral complexes range up to near $1000 \text{ l mole}^{-1} \text{ cm}^{-1}$.

An additional factor in discussing transitions in the

clusters is that a consideration of the d-atomic orbital from which a molecular orbital arises must be made. Strictly, transitions between molecular orbitals arising from various pure d-orbitals would be forbidden on the basis of atomic orbital orthogonality. However, mixing of the d-orbitals with one another and inclusion of p character from either the metal or ligand could provide a mechanism for partially allowing this type of transition¹. Opinions on the intensity expected from this kind of transition vary widely. Mackay (17) as reported above has suggested that the extinction coefficient could be as high as $2000 \text{ l mole}^{-1} \text{ cm}^{-1}$. Robin and Kuebler (7) on the other hand imply that an orbitally forbidden transition in the clusters should have negligible intensity. An example for a different system is found in the discussion of the spectra of $\text{Re}_2\text{Cl}_8^{2-}$ by Cotton and Harris (46). They assigned two bands, at $19,700 \text{ cm}^{-1}$ ($\epsilon=5600$) and $34,800 \text{ cm}^{-1}$ ($\epsilon=8800$) (47), as electric dipole allowed (symmetry allowed) transitions, but the transition at $18,700 \text{ cm}^{-1}$ ($\epsilon=1500$) (47) was assigned as being electric dipole forbidden. These transitions, in the above order, are between the predominately metal

¹These transitions will be designated as either orbitally allowed or forbidden.

one-electron molecular orbitals $b_{2g}(xy) \rightarrow b_{1u}(xy)$, $e_g(xz,yz) \rightarrow a_{2u}(z^2)$, and $b_{2g}(xy) \rightarrow a_{2u}(z^2)$. Note that no account of atomic orbital orthogonality has been taken.

It is apparent, then, that the explicit assignment of the complete cluster spectrum must be regarded as a tenuous task. There is insufficient detail in the calculations which have been made to warrant making complete assignments.

Conclusions regarding the electronic spectra

In concluding the discussion of the electronic spectra of the clusters, some tentative band assignments are considered in light of the previously discussed data and bonding calculations. In Table 9 some possible allowed electronic transitions for the cluster are outlined. Note that Laporte forbidden transitions are not included even though they may be between the representations arising from the same d-orbitals. The order in the table is in approximately ascending energy from top to bottom. The ultraviolet region of the spectrum has been fully discussed earlier in this report and will not be further considered.

In the low energy spectrum there is a sharp band at ca. 10 kK for the niobium 3+ and 4+ clusters. This band appears

Table 9. Possible metal to metal orbital transitions^a

Allowed	LaPorte allowed orbitally forbidden
$a_{2u}(xy) \rightarrow t_{2g}(xy)^b$	$t_{2g}(xz,yz) \rightarrow a_{2u}(xy)^c$
$t_{2g}(xz,yz) \rightarrow t_{2u}(xz,yz)$	$t_{2g}(xz,yz) \rightarrow e_u(xy)$
$t_{1u}(xz,yz) \rightarrow t_{1g}(xz,yz)$	$t_{2g}(xz,yz) \rightarrow t_{1u}(z^2)$
$a_{1g}(z^2) \rightarrow t_{1u}(z^2)$	$t_{1u}(xz,yz) \rightarrow t_{2g}(xy)$
	$t_{1u}(xz,yz) \rightarrow e_g(z^2)$

^aAll transitions are spin allowed.

^bShould occur only for 2+ and 3+ clusters.

^cShould occur only for 3+ and 4+ clusters.

unique to these oxidation states and is seen to correlate well with bands at ca. 12 kK for the 3+ and 4+ tantalum clusters. The band can be tentatively assigned as a transition to the $a_{2u}(xy)$ orbital from the $t_{2g}(xz,yz)$ orbital which is the only formally allowed transition of that type.

In this same spectral region there are then two unique bands in the 2+ and 3+ niobium and tantalum clusters, ca. 10 and 8 kK and ca. 13-15 and 11-14 kK, respectively which correspond as shown earlier. Since they are common to the 2+ and 3+ oxidation states these bands are thought to arise from transitions out of the $a_{2u}(xy)$ orbital into an anti-

bonding metal molecular orbital. Reference to Table 9 will show that only one transition out of the $a_{2u}(xy)$ orbital is allowed, but the bands in question here have approximately equal energies.

Of other possible transitions out of the $a_{2u}(xy)$ orbital, all are LaPorte forbidden but one into the $e_u(xy)$ orbital is between molecular orbitals arising from the same metal d-orbital. The second transition from the $a_{2u}(xy)$ orbital may gain its high intensity through either a vibronic mixing or intensity stealing mechanism (43, p. 204). Either of the above alternatives could explain the intensity of a LaPorte forbidden band. In any case, the point here is that one of the transitions from the $a_{2u}(xy)$ orbital is probably to the $t_{2g}(xy)$ antibonding orbital.

The only bands remaining in the low energy spectrum are at 8.64 and 10.1 kK for the tantalum 4+ cluster and at 8.65 kK for the niobium 4+ cluster. As explained earlier the 10.1 kK tantalum band corresponds to the one at 8.65 kK in niobium. These bands most likely involve transitions into the $a_{2u}(xy)$ orbital since they would be at too low an energy for another assignment. If the above statement is true the analogous transitions also would be expected in the 3+ spectra. How-

ever, they would certainly be buried in the stronger near infrared absorption occurring for that oxidation state and hence be undiscovered.

The relatively low intensity of these bands suggests that they may be forbidden transitions which are allowed only via a mixing or vibronic interaction. There are, in fact, no allowed transitions into the a_{2u} orbital other than from the $t_{2g}(xz,yz)$ which has been discussed above, and also there are only two additional metal orbitals ($t_{1u}(xz,yz)$ and $a_{1g}(z^2)$) at lower energy than the $a_{2u}(xy)$. Assignment of the transitions as being from the latter two orbitals to $a_{2u}(xy)$ involves reordering the Cotton and Haas (27) molecular orbitals so that in descending energy they are: $a_{2u}(xy) > t_{1u}(xz,yz), a_{1g}(z^2) > t_{2g}(xz,yz)$. A justification for this procedure cannot be made at this time, although the detail of the Cotton and Haas ordering (Figure 5) should not be accepted without reservation.

There remain four bands in all three oxidation states of the niobium and tantalum spectra which appear to be metal to metal transitions in view of the criteria used to assign charge-transfer transitions.

One band at ca. 23 kK and ca. 28 kK in the niobium and

tantalum clusters, respectively is much more intense than the other visible bands. This transition must be fully allowed and other than the previously examined transitions from the $a_{2u}(xy)$ orbital is the first or lowest energy allowed metal to metal transition. The assignment $t_{2g}(xz,yz) \rightarrow t_{2u}(xz,yz)$ is suggested but taking a reordering of orbitals into account the assignment of $t_{1u}(xz,yz) \rightarrow t_{1g}(xz,yz)$ is possible.

The two relatively weak bands in the far visible region of the spectrum are evidently only partially allowed. These bands are assigned as metal to metal transitions which are at least partially allowed via a vibronic mechanism because δ was found to decrease on decreasing the temperature. Other effects may be operative to relax selection rules, and consequently no explicit assignments are made for these bands.

The remaining band which is considered to involve a transition between predominately metal molecular orbitals is at ca. 30 kK. It is intense ($\epsilon = 3000 \text{ l mole}^{-1} \text{ cm}^{-1}$ for niobium) but rather weak relative to the 23 kK band. This band may be the next allowed metal to metal transition after the one at 23 kK although its proximity to the charge transfer bands could allow for a magnified intensity stealing and a high intensity for a partially forbidden band.

The above transition possibilities are most plausible in considering transitions to and from the $a_{2u}(xy)$ molecular orbital. The proposed explanations are, in general, not explicit enough to warrant a full semi-empirical orbital ordering proposal, but they do lead to the conclusion that the lowest antibonding orbital lies ca. 7 to 10 kK^1 higher than the highest bonding orbital, $a_{2u}(xy)$. Also, the orbital just below $a_{2u}(xy)$ is 7 to 8 kK^1 lower. In each case, then, it appears as if the remaining antibonding and strongly bonding orbitals lie fairly close in energy. The following order of Cotton and Haas (27) orbitals may be constructed (in order of increasing energy): t_{1u} , a_{1g} , t_{2g} < (by 7-8 kK) a_{2u} < (by 7-10) t_{2g} , e_u , t_{2u} , t_{1g} , e_g , t_{1u} .

An attempt to be more explicit than above would lead to gross assumptions and an untenable position.

As a conclusion to this section it is interesting to look at the implications of the above orbital ordering in terms of the chemical behavior of the clusters. The facile oxidation of the clusters is a certain ramification of the relatively high energy of the a_{2u} orbital. The placement of this orbital

¹The variation is because of oxidation state and metal (tantalum or niobium).

suggests that either reduction of the $M_6X_{12}^{2+}$ cluster or oxidation of the $M_6X_{12}^{4+}$ cluster would be unlikely to occur except under severe reaction conditions.

The proposed orbital ordering shows the a_{2u} orbital to be approximately 1.0 kK higher in the tantalum cluster relative to the next highest energy bonding orbital. This would indicate that oxidation of the tantalum cluster may be slightly more favored than that of the niobium cluster. Mackay (17, p. 31) has reported polarographic data for some niobium and tantalum clusters which is in agreement with the above rationalization.

Far Infrared Spectra

Examination of previous results

The far infrared spectra of a series of niobium cluster complexes and some tantalum cluster complexes has been obtained. It was hoped that by varying the atom components of the clusters that assignment of the bands would be possible. The extensive series of compounds measured in this study would also resolve some of the differences in band assignments reported by earlier workers (17,18,48).

Mackay and Schneider (48) and Mackay (17) utilized a model for the fully coordinated cluster $[(M_6X_{12})Y_6]$ in which

the possible infrared active modes were separated as described below. A similar model was developed by Cotton et al. (49) for treating the far infrared spectra of $[(Mo_6X_8)Y_6]^{2-}$ anions.

For the M_6X_{12} cluster the application of group theory showed that four infrared active T_{1u} modes were expected. It was further proposed (17,48) that if these modes involved primarily motions of the inner cluster halogens or the metal atom octahedron then there would be three metal-halogen inner cluster modes and one metal-metal mode. It was then suggested that the addition of terminal Y ligands introduced two modes, an M-Y stretching mode and an X-M-Y bending mode, which could be interpreted on the basis of an $M'Y_6$ ($M' = M_6X_{12}$) model. If the observed spectra actually corresponded to pure modes such as the above, assignment of the bands would be made relatively easy by comparing cluster derivatives where the M, X, and Y atoms were varied.

However, all of the infrared active modes of the clusters are T_{1u} symmetry and this means that interaction between the modes may take place. The exact form of the interactions between the modes cannot be predicted so that the situation could be obtained where some bands may be ascribed to relatively pure modes of parts of the cluster whereas other bands

result from highly mixed modes. For example it is difficult to qualitatively understand how a nearly pure metal atom mode could result. Resonance interaction can take the form of removing accidental degeneracies and/or varying the intensity of a band from one spectrum to another. The result of significant interaction would lead to spectra that are not understandable in terms of the model developed above.

The detailed results of earlier studies on M_6X_{12} cluster derivatives will be discussed below.

Mackay (17) and Mackay and Schneider (48) have reported far infrared data for some $Nb_6Cl_{12}^{n+}$ ($n = 2,3,4$) derivatives and made qualitative band assignments on the basis of their model discussed above. Data reported for the complexes $R_n[(Nb_6Cl_{12})Cl_6]$ ($R = Et_4N^+$, $n = 2,3,4$) were in agreement with that obtained here for the major peaks. Measurements were also obtained on $R_2[(Nb_6Cl_{12})X_4(EtOH)_2]$ ($X = Cl, Br$), $R_4[(Nb_6Cl_{12})X_6]$ ($X = Br, I$) and $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$ where $R = Et_4N^+$ and N-methylpyridinium for $X = I$. The latter three compounds were incompletely analyzed and their exact composition was questionable.

By comparing the data obtained for their compounds Mackay and Schneider (48) assigned the three highest fre-

quency bands, viz. 340, 280, and 232 cm^{-1} , to inner cluster, $\text{Nb}_6\text{Cl}_{12}$, modes. These band positions were for the 2+ cluster in the 4- anionic derivative, and they were reported to increase by 15-30 cm^{-1} on changing the cluster oxidation state to 4+ in the anionic derivatives.

For the compounds where the terminal ligand was chloride a band which increased in energy as the oxidation state was lowered (opposite to the above behavior) appeared at ca. 200 cm^{-1} . This band was not present when the terminal ligand was changed to bromide and iodide and a new band appeared at 157 cm^{-1} and 100 cm^{-1} for the above cases. These bands were assigned as niobium-terminal halogen stretching modes. The spectrum of the DMSO adduct (439(s), 339(vs), 288(m), and 241(m) cm^{-1}) was used to support the above assignment scheme. In this latter compound the niobium-oxygen stretching mode was assigned at 439 cm^{-1} with the remaining bands belonging to the inner cluster.

A weak band at ca. 145 cm^{-1} which was relatively constant regardless of the terminal ligand was proposed as the Nb_6 infrared active mode. This band was not observed for all the clusters studied by Mackay and Schneider (48).

Meyer (18, p. 37) has reported the far infrared spectra

of some $Ta_6X_{12}^{n+}$ derivatives and made qualitative assignments of bands in the same manner as Mackay and Schneider (48). For the $[(Ta_6Cl_{12})Cl_6]^{n-}$ ($n = 2,3$) anions the two highest energy bands, 330 and 288 cm^{-1} , were assigned as internal cluster modes. The highest frequency band was split into two components in the Et_4N^+ 4+ cluster spectrum. The third strong band in these spectra at 250 cm^{-1} was assigned as the tantalum-terminal chloride stretch on the basis that the spectrum of $(Et_4N)_2[(Ta_6Br_{12})Cl_6]$ showed two bands at 256 and 244 cm^{-1} whereas the highest band for $(Et_4N)_2[(Ta_6Br_{12})Br_6]$ was at 230 cm^{-1} . This latter band also was present when the terminal ligand was chloride and was assigned as the highest frequency internal cluster mode of the bromide cluster. A band corresponding to the one at ca. 200 cm^{-1} for the niobium chloride clusters was not located. Meyer's assignments (18) have a significant difference with Mackay and Schneider's (48) in that the tantalum-terminal chloride stretching frequency is about 60 cm^{-1} higher than that of the niobium-terminal chloride. In general, metal-halogen stretching modes are slightly lower for the more massive metals providing other variables are held constant.

Meyer (18) additionally stated that Mackay's assignment

(17) of the 140 cm^{-1} band as a metal octahedron mode was apparently substantiated in view of the observation of a band in the $134\text{-}146\text{ cm}^{-1}$ range for most of the tantalum clusters. Meyer assigned the tantalum-terminal bromide stretching frequency at 192 cm^{-1} for the hexachloro $4+$ bromide cluster and at 161 cm^{-1} for the hexabromo $4+$ bromide cluster, both of which are higher than the niobium-terminal bromide stretching frequency assignment of Mackay. In the low energy region of the spectrum, Meyer assigned tantalum-terminal halogen modes at 118 cm^{-1} for the chloride and 82 cm^{-1} for the bromide.

Boorman and Straughan (29) have reported the far infrared spectra of a series of niobium and tantalum $2+$ clusters. They did not make specific band assignments and in general, their data were more complex than that reported for anhydrous compounds since they were dealing with mainly hydrated compounds. Their prominent bands have been substantiated in this work wherever there was overlap of effort.

Far infrared data and assignments

The data obtained in this study are reported in Figures 6-9 and Tables 9-11. These data are presented as frequency (cm^{-1}) and tentative assignments arrived at are listed after the bands where possible. The assignments are made as:

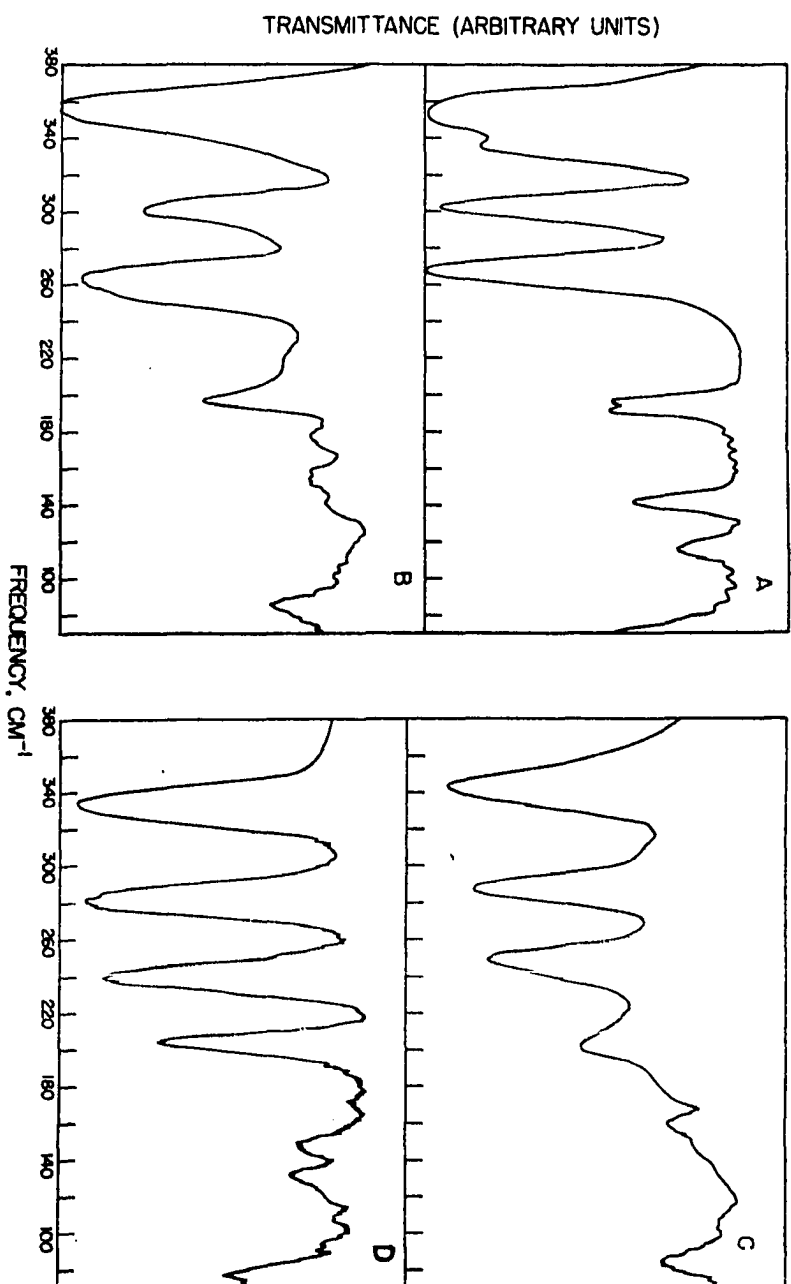


Figure 6. Far infrared spectra of some $R_n[(Nb_6Cl_{12})Cl_6]$

- A. $[Et_4N]_2[(Nb_6Cl_{12})Cl_6]$
- B. $[n\text{-}prNH_3]_2[(Nb_6Cl_{12})Cl_6]$
- C. $[n\text{-}prNH_3]_3[(Nb_6Cl_{12})Cl_6]$
- D. $[Me_4N]_4[(Nb_6Cl_{12})Cl_6]$

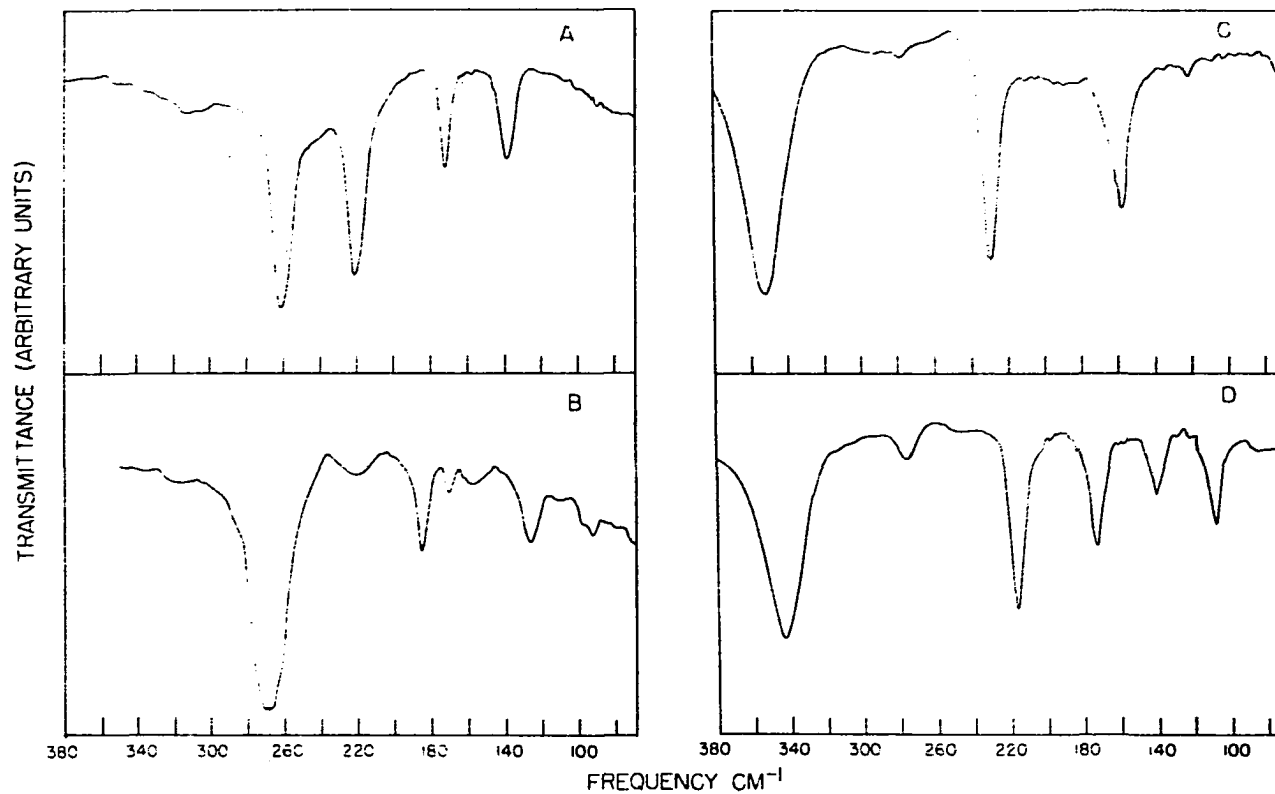


Figure 7. Far infrared spectra of some $R_n[(Nb_6X_{12})Y_6]$ complexes

A. $[n\text{-bu}_4\text{N}]_2[(Nb_6Br_{12})Br_6]$.
 B. $[Et_4N]_2[(Nb_6Br_{12})Cl_6]$.
 C. $[n\text{-prNH}_3]_2[(Nb_6Cl_{12})Br_6]$.
 D. $[n\text{-bu}_4\text{N}]_3[(Nb_6Cl_{12})I_6]$.

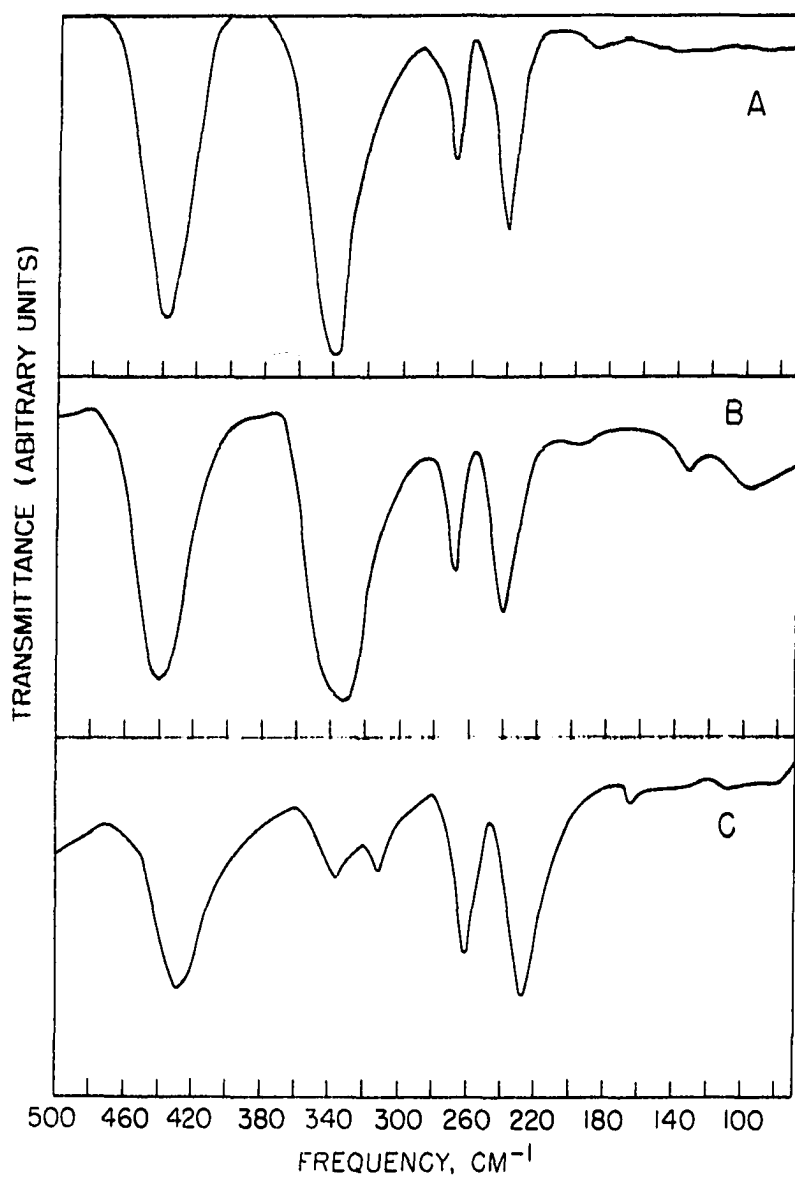


Figure 8. Far infrared spectra of some $\text{Nb}_6\text{X}_{12}^{2+}$ DMSO adducts
 A. $[(\text{Nb}_6\text{Cl}_{12})(\text{DMSO})_6](\text{ClO}_4)_2$
 B. $[(\text{Nb}_6\text{Cl}_{12})\text{Br}_2(\text{DMSO})_4]$
 C. $[(\text{Nb}_6\text{Br}_{12})(\text{DMSO})_6](\text{ClO}_4)_2$

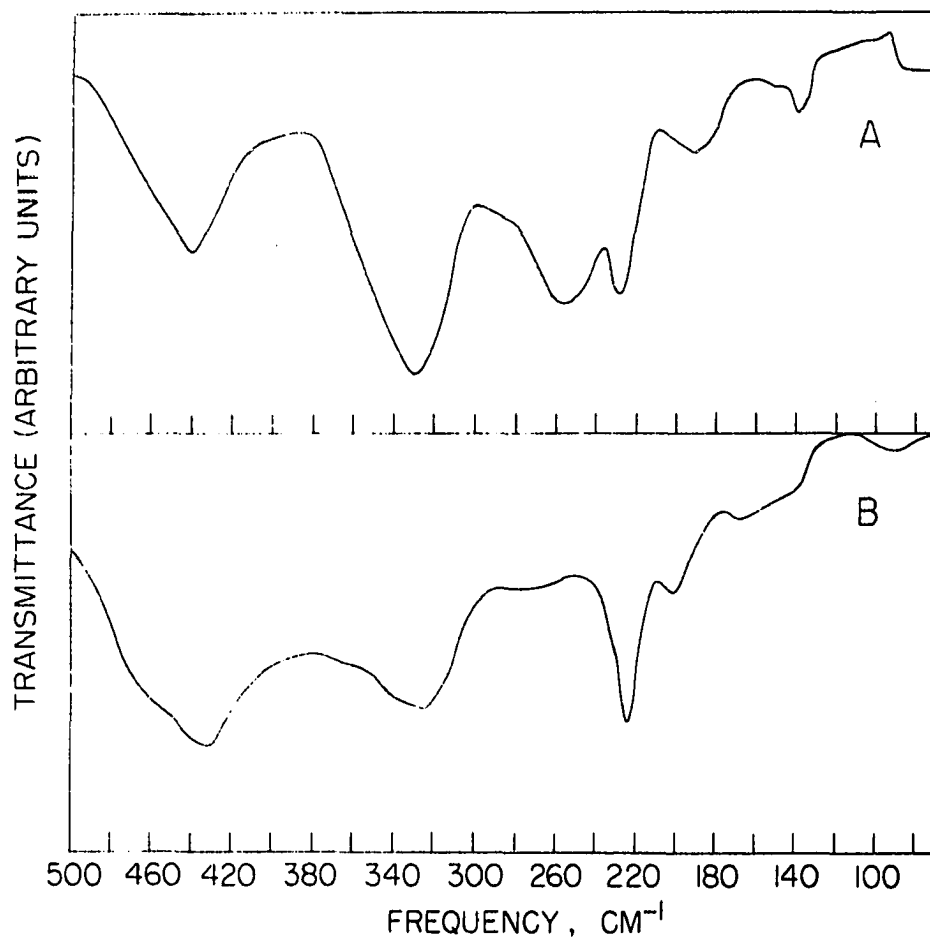


Figure 9. Far infrared spectra of some $\text{Ta}_6\text{Cl}_{12}^{3+}$ DMSO adducts
A. $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_3(\text{DMSO})_3]$
B. $[(\text{Ta}_6\text{Cl}_{12})(\text{DMSO})_6](\text{ClO}_4)_3$

Table 9. Far infrared spectra of some $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$ anions

$\text{R}_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$		$\text{R}_3[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$		
$\text{R} = \text{Et}_4\text{N}^+$	$\text{R} = \text{n-prNH}_3^+$	$\text{R} = \text{Et}_4\text{N}^+$	$\text{R} = \text{n-prNH}_3^+$	$[\text{Me}_4\text{N}]_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$
354(vs) ^a _i ^b	357(vs) _i	343(vs) _i	343(vs) _i	334(vs) _i
336(s) _i	--	--	--	--
302(vs) _t	300(s) _t	290(vs) _t	287(vs) _t	281(vs) _t
267(vs) _i	263(vs,b) _i	252(vs) _i	249(vs) _i	239(vs) _i
196(s) _{mt}	196(s) _{mt}	198(ms) _{mt}	200(m) _{mt}	203(vs) _{mt}
190(s) _{mt}	--	--	--	--
--	176(w)	--	--	--
--	154(w)	--	158(w)	--
142(s)	141(vw)	141(w)	--	147(mw)
115(m)	--	122(w)	--	132(w)
--	85(m)	--	83(m)	--
71(m)	--	70(vw)	--	77(w)
64(w)	--	64(vw)	--	64(m)

^aBand positions are in cm^{-1} . Relative intensities are: s=strong, m=medium, w=weak, v=very, b=broad, sh=shoulder.

^bBand assignments: i=internal M_6X_{12} mode; t=terminal M-Y mode; mt=mode containing metal and terminal ligand contribution; nt=terminal halogen impurity.

Table 10. Far infrared of some $[(\text{Nb}_6\text{X}_{12})\text{Y}_6]^{n-}$ anionic derivatives

$\text{R}_2[(\text{Nb}_6\text{Br}_{12})\text{Br}_6]$					
$\text{R}=\text{n-Bu}_4\text{N}^+$	$\text{R}=\text{n-prNH}_3^+$	I ^a	II ^b	III ^c	IV ^d
				595(m,sh) ^e _t	
				575(s) _t	
				552(s) _t	
				430(vs,b)	
			352(vs) _i	320(vs,b) _i	343(vs) _i
			276(vw)	278(w) _{nt}	276(w) _{nt}
262(vs) _i	262(s) _i	268(vs,b) _{i,t}			
220(vs) _t	219(s) _t	219(w) _{nt}	228(vs) _{t,i}	236(w) _i	216(vs) _i
		184(ms) _{mt}		205(vw) _{mt}	
171(s) _i	172(m) _i	169(w) _i		171(w)	172(s) _t
		156(w) _{nt}	157(s) _{mt}		
138(s) _{mt}	140(m,b) _{mt}				141(m)
		126(ms)			
	59(w)	93(w)			108(s) _{mt}

^aI=[Et₄N]₂[(Nb₆Br₁₂)Cl₆].

^bII=[n-prNH₃]₂[(Nb₆Cl₁₂)Br₆].

^cIII=[Et₄N]₄[(Nb₆Cl₁₂)F₆].

^dIV=[n-bu₄N]₃[(Nb₆Cl₁₂)I₆].

^eFrequencies, intensities, and assignments are as in Table 9.

Table 11. Far infrared spectra (500-70 cm^{-1}) of some DMSO adducts of M_6X_{12}

I ^a	II ^b	III ^c	IV ^d	V ^e	VI ^f
435(vs) ^g t	437(vs)t	440(vs)t	429(vs)t	440(s)t	433(s,b)t
338(s,b)i	340(vs)i	334(vs,b)i	337(w)	330(vs,b)i	325(ms,b)i
290(s,b)t	---	---	312(w)	262(m)t	---
252(s)i	270(ms)i	268(ms)i	262(vs)i	247(m,sh)i	
240(m,sh)mt	240(s)mt	240(s)mt	229(vs)mt	227(m)mt	224(s)mt
198(mw)mt	---	196(vw)t	---	192(w)	199(w)
118(vw)	---	133(vw)mt	165(w)i	140(w)	145(w)

^aI = $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_3(\text{DMSO})_3]$. This compound was prepared, analyzed, and infrared obtained by W. Grindstaff of this laboratory.

^bII = $[(\text{Nb}_6\text{Cl}_{12})(\text{DMSO})_6][\text{ClO}_4]_2$.

^cIII = $[(\text{Nb}_6\text{Cl}_{12})\text{Br}_2(\text{DMSO})_4]$.

^dIV = $[(\text{Nb}_6\text{Br}_{12})(\text{DMSO})_6]$.

^eV = $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_3(\text{DMSO})_3]$.

^fVI = $[(\text{Ta}_6\text{Cl}_{12})(\text{DMSO})_6][\text{ClO}_4]_3$.

^gFrequencies, intensities, and assignments are as in Table 9.

i) a mode consisting mainly of motion of the internal halogen atoms of the cluster, t) a mode involving mainly motion of the terminal halogen atoms, or mt) a mode involving significant contributions of both metal and terminal halogen motion. The certainty of the individual assignments is discussed below along with a consideration of the experimental spectra.

In approaching the interpretation of these spectra it has been assumed a priori that the niobium and tantalum cluster data should exhibit the same general features. It was felt that there should be a 1:1 correspondence in the number of bands, and that frequency changes between the two clusters should not be great except perhaps if a band arose from a mode containing a large metal contribution. This assumption was made on the basis of the similarities in molecular and electronic structure discussed in the electronic spectra section.

The spectra of the $R_n[(Nb_6Cl_{12})Cl_6]$ complexes (Table 9 and Figure 6) all show the same general feature of four strong absorptions at greater than ca. 200 cm^{-1} . The three highest bands show a decrease in energy as the cluster oxidation state is lowered which is in accord with what would be expected.

The band at ca. 200 cm^{-1} increases in frequency slightly as oxidation state decreases. In the lower energy region of the spectrum there are several bands at different energies depending on whether the cation is Et_4N^+ or n-prNH_3^+ . In view of the inability to duplicate these bands they are not considered as cluster fundamentals. In fact the region below 140 cm^{-1} is generally a difficult one to assign bands in due to the appearance of lattice modes and consequently is regarded with suspicion.

Note in Table 9 and Figure 6 that in the Et_4N^+ 4+ complex the highest energy band is split with a defined shoulder at 336 cm^{-1} and also the lowest energy strong band is split into peaks at 196 and 190 cm^{-1} . Mackay and Schneider (48) did not observe this behavior. The 3+ Et_4N^+ salt does not exhibit this splitting. It is interesting that Meyer (18) has observed the identical phenomenon in the 3+ and 4+ hexachloro tantalum chloride clusters. The highest energy band in the 4+ cluster exhibits a defined shoulder at 318 cm^{-1} which is exactly the same shift seen for the niobium cluster.

There is not an obvious tantalum analog to the relatively strong niobium band at ca. 200 cm^{-1} but in view of the similarities in the properties of the clusters there should be

such a band. The weak two component band at 160 and 164 cm^{-1} is the most reasonable choice. These bands coalesce to one weak band at 171 cm^{-1} in the $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]^{3-}$ anion which is the behavior noted in the niobium spectra. Meyer¹ has recently obtained a spectrum of a 2+ hexachloro cluster derivative which exhibits a weak band at 180 cm^{-1} . Thus, the anomaly of apparently only three major bands existing in the $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$ far infrared spectra as compared to four in the $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$ spectra is solved. The reason for the intensity of the tantalum bands being so low relative to the niobium bands is not understood.

These bands are the only ones in the spectra that increase in frequency as the cluster oxidation state is decreased. Also, along with the highest energy bands in the spectra i.e., 352, 343, and 334 cm^{-1} for $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$ ($n = 2, 3, 4$), these bands are at much lower energy (23-30 cm^{-1}) for tantalum. These facts suggest that the bands result from a mode that has a significant metal atom contribution. The highest energy bands which are assigned later as primarily internal cluster vibrations would also have a metal atom contribution by the above criteria.

¹Meyer, J. L. Ames, Iowa. The infrared spectra of some new 2+ tantalum cluster complexes. Private communication. 1968.

Further examination of the low energy spectrum shows that Meyer (18) has observed bands at 140 and 118 cm^{-1} for the 3+ and 4+ hexachloro tantalum clusters. These band positions are identical to those obtained here for the Et_4N^+ complexes (Table 9, Figure 6).

In Table 10 and Figure 7 far infrared spectra of some additional anionic cluster derivatives are reported. The four bands observed for $[(\text{Nb}_6\text{Br}_{12})\text{Br}_6]^{2-}$ correspond to the bands of the $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{n-}$ anions. All of the bands are ca. 0.7 the energy of the chloride bands. This ratio is in good agreement with the general ratio $\nu(\text{Br})/\nu(\text{Cl}) = 0.7$ where ν denotes a stretching mode (49). These bands also correspond much more obviously to the four highest energy bands (230, 196, 161, 134 cm^{-1}) reported by Meyer (18) for $[\text{Et}_4\text{N}]_2 [(\text{Ta}_6\text{Br}_{12})\text{Br}_6]$ than in the hexachloro chloride spectra.

The spectrum of the $[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]^{2-}$ anion is puzzling. The presence of a band at 352 cm^{-1} establishes the highest energy band as due to the $\text{Nb}_6\text{Cl}_{12}$ cluster. This is borne out in the bromide cluster system where the band at 262 cm^{-1} is the highest internal cluster frequency. This highest frequency band does not show a large dependence on the type of terminal ligand but does vary with charge (Table 9, Figure 6).

The remainder of the hexabromo chloride cluster spectrum has two bands, 228 and 157 cm^{-1} . This is a loss of one band compared to the hexachloro chloride and differs from the data reported by Mackay and Schneider (48) for $(\text{Et}_4\text{N})_4[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$ (347(vs), 280(m), 228(s), 157(ms) and 148(sh)). These differences are not easily explained although the band at 280 cm^{-1} may result from impurity in Mackay's compound since he made his material from $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2 \cdot n\text{H}_2\text{O}$ rather than the dibromo chloride hydrate. One of the two bands observed here should be a niobium terminal bromide stretching mode. The spectrum of the hydrate $[\text{Nb}_6\text{Cl}_{12}]\text{Br}_2 \cdot 7\text{H}_2\text{O}$ has bands at 364(vs), 343(s), 262(vw), 232(vs), 196(ms), 151(s), and 127 cm^{-1} which agrees with that of the anhydrous complex except for the extra 196 and 127 cm^{-1} bands. This hydrate spectrum was helpful in confirming the absence of strong bands between 230 cm^{-1} and 340 cm^{-1} . This suggests that the niobium-terminal chloride stretching frequency is in this region, but the anomalously small number of bands in the anhydrous complex is not explained, especially in view of resonance phenomenon which should split accidental degeneracies.

In an effort to establish a band for the niobium-terminal chloride stretch the spectrum of $(\text{Et}_4\text{N})_2[\text{Nb}_6\text{Br}_{12}\text{Cl}_6]$ was

obtained. This previously unreported compound was prepared by the addition of solid Et_4NCl to an ethanol solution of $[\text{Nb}_6\text{Br}_{12}]\text{Br}_2 \cdot 8\text{H}_2\text{O}$ saturated with hydrogen chloride after oxidation of the cluster with chlorine. The spectrum is reported in Table 10. The strong band at 268 cm^{-1} is judged to contain two bands because of its broadness. The bands correspond to the 262 cm^{-1} internal bromide cluster mode and a band at ca. 270 cm^{-1} which is assigned as the terminal chloride stretch in this compound. This frequency is ca. 15 cm^{-1} higher than for the corresponding band established by Meyer (18) in the analogous tantalum complex.

The hexaiodo niobium chloride cluster (Table 10) shows the high energy internal cluster band which is not shifted from its position in the hexachloro cluster. The spectrum is similar to the hexabromo spectrum down to 200 cm^{-1} but shows the new band at 172 cm^{-1} and a strong band at 108 cm^{-1} which may be the terminal iodide stretching frequency. The band at 216 cm^{-1} appears to correspond to the 228 cm^{-1} band in the hexabromo chloride cluster suggesting that it is an internal cluster mode. Generally one expects $\nu(\text{I})/\nu(\text{Br})$ of ca. 0.8 and if this relation holds the Nb-Br stretching frequency could be assigned at 157 cm^{-1} and the Nb-I stretching

frequency at 108 cm^{-1} . The 216 cm^{-1} (hexaiodo) and 228 cm^{-1} (hexabromo) bands could then be assigned as arising from an internal cluster mode with some terminal ligand contribution which would act to lower the band frequency in the order $\text{Cl} > \text{Br} > \text{I}$.

In examining the various spectra, however, an alternative assignment scheme was arrived at, and this is the one reported in Tables 6-9. This scheme is favored since it can account for a larger part of the spectra.

In this case, the 172 cm^{-1} band of the hexaiodo cluster could be considered as arising from terminal iodine vibrations. This would suggest 228 cm^{-1} as the terminal bromide mode. The 108 and 157 cm^{-1} bands could still be assigned as having large terminal ligand contributions. In order to follow this correlation further bands at 300 and 200 cm^{-1} in the hexachloro chloride cluster would be assigned as the terminal chloride stretch and a mode involving metal atom and terminal ligand contribution, respectively. This scheme is consistent with the data obtained on the DMSO complexes which are discussed later. In fact, the DMSO complexes yielded evidence which strongly supports the above scheme.

The data obtained for the hexafluoro $2+$ chloride cluster

is included in Table 10 for completeness. This spectrum was not well resolved, and the purity of the compound is questionable as the analysis showed. There are two regions of absorption at higher energies, 575 and 430 cm^{-1} , which are apparently associated with the terminal fluoride ligand. The highest absorption can be assigned as the Nb-F stretching mode. The 430 cm^{-1} region is high for a bending frequency and could be a mixed mode of the internal cluster and terminal fluoride. The 320 cm^{-1} band is the strong high frequency $\text{Nb}_6\text{Cl}_{12}$ mode. Other weak bands are observed at the energies of the hexachloro chloride cluster bands (Table 9) suggesting the possibility of terminal chloride impurity and more significantly serious intensity variations of internal cluster modes upon changing the terminal ligand.

In Table 11 and Figures 8 and 9 data obtained for some DMSO adducts of some clusters are reported. The preparative methods for these clusters are briefly described here. The hexakis DMSO adducts (compounds II, IV, and VI in Table 11) were synthesized by dissolving the appropriate cluster hydrate in a minimum volume of DMSO, adding excess silver perchlorate, and stirring overnight. The silver halide precipitate was filtered off and the cluster complex was isolated by the

addition of chloroform. The complex was isolated on filter paper, washed with ethanol and ether and air dried. These perchlorate compounds were found to be shock sensitive, but small amounts could be handled normally with caution.

Compounds III and V in Table 11 were synthesized by dissolving the appropriate hydrate in DMSO, adding chloroform and ether and isolating the compound on a sintered glass frit. These complexes were not analyzed but infrared data indicated they were the desired material. The compound $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_3(\text{DMSO})_3]$ was prepared, analyzed, and the infrared spectrum obtained by W. K. Grindstaff¹.

All of the DMSO adducts have a strong band in the range $429\text{-}440\text{ cm}^{-1}$ which is assigned as the metal-oxygen stretch of coordinated DMSO. This is in accord with Mackay and Schneider's (48) observation of the Nb-O stretch 439 for their hexakis DMSO adduct of the 2+ chloride cluster. Field and Kepert (19) had reported the Nb-O stretch at $417\text{-}449\text{ cm}^{-1}$ in the spectra of their series of oxygen donor complexes. Other workers (50) have reported that for a large series of metal DMSO complexes the band(s) in the region $410\text{-}500\text{ cm}^{-1}$ are due

¹Grindstaff, W. K. Ames, Iowa. Preparation and infrared spectra of DMSO adducts of $\text{Nb}_6\text{Cl}_{12}^{3+}$. Private communication. 1967.

to metal-oxygen stretching vibrations. There are several points that are brought out by discussing this band position. One, the metal-oxygen stretching frequency is in the same region as it is for other metal coordination compounds. This suggests that, in general, the terminal ligand stretching modes for the cluster compounds may be in the same frequency region as for other complexes. The band assignments in Tables 6-9 reflect this idea. Two, the metal-oxygen stretching frequency is not highly sensitive to the metal and halogen in the cluster. In fact this band is lowest for the $\text{Nb}_6\text{Br}_{12}$ cluster. These facts indicate that the terminal ligand stretching frequency should be of nearly the same frequency for the niobium and tantalum clusters.

In all of the DMSO adducts the high frequency band which has been assigned as an internal cluster mode is present. This band is generally broad and in the case of the $\text{Nb}_6\text{Br}_{12}$ hexakis DMSO complex there are bands at 337 and 312 cm^{-1} in addition to the 262 cm^{-1} internal cluster mode. The former two bands are due to free DMSO which was retained in the complex.

A band in the 224 to 240 cm^{-1} region appears to grow into the spectra of the DMSO complexes. For example the 240

cm^{-1} band increases intensity as one, two, and three DMSO ligands replace chloride¹. This is shown for the tris DMSO niobium chloride cluster in Table 11. This band is at ca. 240 cm^{-1} for $\text{Nb}_6\text{Cl}_{12}^{n+}$ complexes, 229 cm^{-1} in the $\text{Nb}_6\text{Br}_{12}^{2+}$ complex and at ca. 225 cm^{-1} for the $\text{Ta}_6\text{Cl}_{12}^{3+}$ complexes. The band is assigned as a mode involving a large terminal ligand contribution and may correspond to the other low terminal ligand modes assigned in Tables 9-11 as mt modes. As noted earlier the terminal ligand dependency of the 200 cm^{-1} band of the hexachloro anions is illustrated in these DMSO complexes.

The remainder of the spectra of the hexakis DMSO adducts exhibits only one band which is at 270 cm^{-1} for the $\text{Nb}_6\text{Cl}_{12}$ clusters and 165 cm^{-1} for the $\text{Nb}_6\text{Br}_{12}$ cluster. This band is assigned as the other internal cluster mode which is observed in the hexahalo cluster species. The band is at somewhat higher energy than might be expected for the niobium chloride clusters but in this case resonance with the 240 cm^{-1} band could act to give this shift.

As noted earlier Mackay and Schneider assign all the

¹Grindstaff, W. K. Ames, Iowa. Preparation and infrared spectra of DMSO adducts of $\text{Nb}_6\text{Cl}_{12}^{3+}$. Private communication. 1967.

bands at lower frequency than the Nb-O stretch to internal cluster modes and they have reported a band at 288 cm^{-1} rather than 270 cm^{-1} . The data obtained here strongly indicate that the band at 240 cm^{-1} is associated with the coordinated DMSO.

Summary of infrared results

The assignments proposed in Tables 9-11 are offered as a plausible rationalization of the spectra. It is realized, however, that interaction of the T_{1u} modes of the cluster make these assignments approximate at best.

The assignments here differ markedly from those of Mackay and Schneider (48) in that the niobium-terminal halogen stretching frequency is higher and no pure metal mode is assigned. There is agreement in that the 200 cm^{-1} band of the hexachloro chloride cluster is thought to involve significant terminal ligand character although this frequency is not the terminal chloride stretching frequency.

The assignments of Meyer (18) are in closer agreement with those obtained here. However, in the hexachloro chloride cluster the tantalum-terminal halogen stretching mode would be moved up to 294, 283, and 275 cm^{-1} for the 4+, 3+, and 2+ clusters. This assignment suggests that the internal halogen has a considerable effect on the terminal halide

stretching frequency with Nb-Cl and Ta-Cl stretching modes at ca. 35 cm^{-1} lower for the bromide cluster compared to the chloride cluster.

Previously unassigned bands in the tantalum spectra are the weak lower energy bands assigned now as due to modes involving combinations of metal and terminal ligand vibration. Some revisions of other assignments would have to be made to bring the tantalum and niobium spectra into correspondence.

SUGGESTIONS FOR FUTURE WORK

A large number of possibilities exist for the synthesis of new M_6X_{12} derivatives. Reactions of the cluster with neutral donor ligands and anions under conditions similar to those used in this work would certainly lead to new complexes. However, as interesting as these possibilities are, new coordination compounds may, in general, not be particularly useful in understanding the molecular and electronic structure of the cluster.

New work in the area of synthetic chemistry of the clusters should be approached from the standpoint of attempting to alter the electronic structure of the M_6X_{12} cluster itself. Work of this type includes the possibilities of partial substitution of the metal atoms or inner halogen atoms. Also, the addition of an atom such as hydrogen into the center of the cluster may be possible in view of the preparation of $[H Nb_6 I_8] I_3$ by Simon (51).

In order to proceed with the understanding of the electronic spectra of the clusters detailed molecular orbital calculations could be of great use. Calculations and a more complete understanding of the effects of non-equivalent terminal ligands and distortions of the metal atom octahedron

will be facilitated by the completion of single crystal x-ray studies, especially on the hexahalo cluster anions.

Some more definite conclusions regarding the far infrared spectra may be possible by obtaining the spectra of new derivatives, especially Ta_6I_{12} compounds. Of course, the preparation of a complex derivative of the Nb_6F_{12} cluster could be invaluable and further efforts to obtain such a compound may be worthwhile. In order to effectively solve the cluster vibration problem, Raman data should be obtained on at least one complex ($Ta_6Cl_{12}^{4+}$ complexes are the best prospects) and then normal coordinate analysis calculations carried out.

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