

level with four d-d bands being observed. This could explain the band observed as a shoulder at 15.3 kK in the spectrum of dodecahedral  $\text{NbCl}_4(\text{diars})_2$ .

**Electron Paramagnetic Resonance Spectrum.**—From the epr spectrum of the chloride it was possible to obtain  $g_{\perp} = 1.98$  and  $g_{\parallel} = 1.80$  from which the average  $g$  value of 1.92 gave a moment of 1.67 BM, only slightly higher than the value 1.60 BM obtained experimentally. With an Archimedean antiprism as a model it has generally been found that  $g_{\parallel} > g_{\perp}$ ,<sup>11,13</sup> while for a triangular dodecahedron usually  $g_{\parallel} < g_{\perp}$ .<sup>11,12</sup>

### Conclusions

Contrary to the report of Clark and Errington,<sup>4</sup> 2,5-dithiahexane is capable of forming eight-coordinate adducts. Since  $\text{TiCl}_4$ ,  $\text{VCl}_4$ , and  $\text{SnCl}_4$  are liquids it is possible that in the homogeneous reaction medium the low solubility of the 1:1 (acceptor:donor) adduct favors its formation; the effective radius of the metal atom or more limited participation of d orbitals may also be important factors. The paramagnetic behavior of  $\text{NbX}_4(\text{dth})_2$  seems to rule out a "topochemical" reaction in which the tetrahalides react without breakdown of their diamagnetic structures.

In addition to the stoichiometry of the complexes, the eightfold coordination and bidentate character of

the ligands are clearly indicated by the spectra. Evidence from the infrared spectra shows that the coordinated dithiahexane adopts the *gauche* conformation, which is in contrast to the predominant *trans* conformation of the free ligand. The bidentate coordination of the ligand thus is indicated since the *gauche* conformation is required for coordination of both sulfur atoms to the same metal atom. The far-infrared results further suggest that the TGT form of the ligand is coordinated. This observation contrasts with the conclusion that the GGG form exists in the gaseous and liquid states.<sup>8</sup> However, the spectra in the region 600–1300  $\text{cm}^{-1}$  suggest that molecular forms around the two C-S bonds can affect the bands occurring in this region, and the doublets which we have observed may be indicative of the presence of both the TGT and GGG forms.

Finally, the decrease of  $\nu(\text{Nb-X})$  by 30 to 50  $\text{cm}^{-1}$  relative to six-coordinate niobium(IV) adducts corroborates the higher coordination number of the metal atom in the compounds reported here. Both the electronic spectra and magnetic properties are in accord with an eight-coordinate, triangular dodecahedral configuration about niobium. On the basis of these results and those reported for the ligand *o*-phenylenebis(dimethylarsine)<sup>3</sup> we expect that other bidentate ligands with heavy donor atoms should promote higher coordination numbers when coordinated to the earlier, heavy transition metal ions.

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## Chemistry of Polynuclear Metal Halides. III. Synthesis of Some Niobium and Tantalum $\text{M}_6\text{X}_{12}^{n+}$ Cluster Derivatives<sup>1</sup>

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Synthetic methods are given for the preparation of hydrated halides and halo complexes of the  $\text{Nb}_6\text{X}_{12}^{n+}$  and  $\text{Ta}_6\text{X}_{12}^{n+}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) clusters in each of the stable oxidation states  $n = 2, 3, \text{ or } 4$ . Most of the compounds were crystallized from aqueous or alcohol solutions containing hydrogen halide for the cases where  $n = 3$  or 4. Difficulties associated with oxidation and solvation of  $n = 2$  derivatives made it desirable to prepare salts of the anions  $(\text{M}_6\text{Cl}_{12})\text{Cl}_6^{4-}$  ( $\text{M} = \text{Nb}$  or  $\text{Ta}$ ) by reduction of the anhydrous chlorides  $\text{MCl}_5$  in the presence of alkali metal chloride at high temperature.

### Introduction

This paper deals entirely with syntheses of many different derivatives containing the basic cluster units  $\text{M}_6\text{X}_{12}^{n+}$ , where  $\text{M} = \text{Nb}$  or  $\text{Ta}$  and  $\text{X} = \text{halogen}$ . Work on the structure, infrared spectra, magnetic properties, and electronic spectra will be published subsequently. These studies are part of a concerted program to understand the important features of the structure and bonding of the hexanuclear metal cluster compounds.

The early literature on the niobium and tantalum cluster containing compounds has been summarized in recent papers on new or improved preparative methods for formation of the basic  $\text{Ta}_6\text{X}_{12}^{2+}$  and  $\text{Nb}_6\text{X}_{12}^{2+}$  cluster units.<sup>2,3</sup> Subsequently it has been shown that both the tantalum<sup>4,5</sup> and niobium<sup>6</sup> clusters may assume

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

three different oxidation states to provide derivatives<sup>6</sup> of  $M_6X_{12}^{n+}$  ( $n = 2, 3, 4$ ). Mackay and Schneider have reported several anionic niobium cluster complexes of the type  $(Nb_6Cl_{12})X_6^{n-}$  ( $X = Cl, Br; n = 2, 3, 4$ ) or of the type  $(Nb_6Cl_{12})X_{2+n}L_{4-n}^{n-}$  ( $X = Cl, Br; L = H_2O, C_2H_5OH$ , or  $(CH_3)_2SO; n = 0$  or  $2$ ) in their work on the magnetic properties<sup>7</sup> and infrared spectra.<sup>8</sup> Other complexes with neutral donor ligands also have been reported.<sup>9</sup>

Only a few complex derivatives of the  $Ta_6X_{12}^{n+}$  clusters have been reported. Among the more important of these are the hydrated derivatives  $(Ta_6X_{12}) \cdot X_2 \cdot nH_2O$  ( $n = 8, 9$ )<sup>10,11</sup> and  $(Ta_6X_{12})X_3 \cdot 7H_2O$ <sup>12</sup> which may be obtained from aqueous solutions. The structure reported for  $(Ta_6Cl_{12})Cl_2 \cdot 7H_2O$  (even though the correct formulation<sup>10</sup> may be  $(Ta_6Cl_{12})Cl_2 \cdot 8H_2O$ ) shows that four water molecules and two chloride ions are coordinated to the cluster unit.<sup>13</sup> Hence the general formulation of these hydrated derivatives as  $[(M_6X_{12}) \cdot X_2(H_2O)_4] \cdot nH_2O$  is indicated.

#### Experimental Section

**Materials.**—In the case of the synthesis of niobium cluster complexes the hydrates  $(Nb_6X_{12})X_2 \cdot 8H_2O$  ( $X = Cl, Br$ ), which were generally used as starting materials, were prepared as described previously.<sup>9</sup> The anhydrous compounds  $Ta_6X_{14}$  ( $X = Cl, Br$ )<sup>2</sup> were used to prepare the tantalum complexes. All other reagents and solvents were of reagent grade and used without purification.

**Tantalum Complexes. Preparation of  $[(Ta_6Br_{12})Br_4(H_2O)_2] \cdot 3H_2O$ .**—Anhydrous  $Ta_6Br_{14}$  (2–3 g) was refluxed in methanol (400 ml) to yield a dark, emerald green solution, which was subsequently centrifuged and filtered to remove an insoluble black residue believed to be tantalum metal. The solution then was oxidized with bromine water and acidified with concentrated HBr (1 ml of acid/40 ml of solution). After reducing the volume to 150 ml by distillation, the solution was cooled, and the jet black fine crystals of product were isolated by filtration. The product was washed with methanol and ether and then dried in air. *Anal.* Calcd for  $Ta_6Br_{16}(H_2O)_3$ : Ta, 44.22; Br, 52.10;  $H_2O$ , 3.67. Found: Ta, 44.30; Br, 51.82;  $H_2O$  (by difference), 3.88; Br:Ta, 2.65.

**Preparation of  $[(Ta_6Cl_{12})Cl_4(H_2O)_2] \cdot 7H_2O$ .**—A sample of  $Ta_6Cl_{14}$  was dissolved in boiling water, cooled to room temperature, and filtered three times through medium-porosity paper to separate an insoluble black residue. The resulting dark blue-green solution was made 3 M in HCl and oxidized by bubbling chlorine through the solution. A red-brown precipitate formed immediately. This product was isolated on a sintered-glass filter, washed with water, and dried in air. *Anal.* Calcd for  $Ta_6Cl_{16}(H_2O)_3$ : Ta, 59.80; Cl, 31.26;  $H_2O$ , 8.93. Found: Ta, 59.95; Cl, 31.01;  $H_2O$  (by difference), 9.04; Cl:Ta, 2.64.

**Preparation of  $H_3[(Ta_6Cl_{12})Cl_6] \cdot nH_2O$ .**—A concentrated solution of  $Ta_6Cl_{14}$  was prepared by refluxing for 6 hr several grams of the anhydrous solid with methanol. This solution was centrifuged and filtered to remove insoluble material; after adding 10 ml of concentrated hydrochloric acid the solution was saturated with gaseous hydrogen chloride and oxidized by bubbling chlorine gas through the solution for 2–3 min. The deep red solution was evaporated at the boiling point until the first appearance of sparkling red crystals. Slow cooling of the solution to ice tem-

perature provided a highly crystalline product and almost colorless mother liquor. The red crystals were filtered by suction, washed with concentrated hydrochloric acid, and dried in a desiccator over KOH. *Anal.* Calcd for  $H_3[(Ta_6Cl_{12})Cl_6] \cdot 6H_2O$ : Ta, 59.20; Cl, 34.80. Found: Ta, 59.2; Cl, 34.5; Cl:Ta, 2.98.

The hydrate number of this compound depends on the method of drying. After drying *in vacuo* for 24 hr the above material lost water and the analysis corresponded to a pentahydrate. Prolonged drying (several days) *in vacuo* leads to further decomposition and loss of HCl. A compound corresponding to  $(Ta_6Cl_{12})Cl_2(OH)_2$  has been obtained by this procedure.

Proof of the formulation of this compound was provided by acid-base titration and ion-exchange methods. Samples of the compound dissolved in methanol were titrated with standard NaOH to the potentiometric end point using a pH meter and glass and calomel electrodes. A sharp end point at 1.95 mol of NaOH/mol of compound resulted. A solution of the compound in 50% aqueous methanol passed through a cation-exchange resin, but the solute was so strongly held by a strong anion-exchange resin that it could not be readily eluted.

**Preparation of  $[(Ta_6Cl_{12})Cl_3(H_2O)_3] \cdot 3H_2O$ .**—An aqueous solution of  $Ta_6Cl_{12}^{2+}$  was titrated spectrophotometrically with aqueous Fe(III) or chlorine until the conversion to  $Ta_6Cl_{12}^{3+}$  was complete, as measured by the disappearance of the strong band at 640 nm, which is characteristic of  $Ta_6Cl_{12}^{2+}$ . The solution was made 0.1 M in HCl and slowly evaporated until precipitation of the product was nearly complete. The fine crystalline product was filtered, washed with dilute HCl, and dried *in vacuo* for 8 hr at room temperature. *Anal.* Calcd for  $Ta_6Cl_{15}(H_2O)_3$ : Ta, 62.92; Cl, 30.82. Found: Ta, 63.0; Cl, 30.9; Cl:Ta, 2.50.

**Preparation of  $[(Ta_6Br_{12})Br_3(H_2O)_3] \cdot 3H_2O$ .**—This compound was prepared in exactly the same way as the above chloride except that aqueous  $Ta_6Br_{12}^{2+}$ , aqueous bromine, and hydrobromic acid were used as reactants. During evaporation of the  $Ta_6Br_{12}^{3+}$  solution the temperature must be held below 50° in order to prevent excessive decomposition of the cluster ion. The black crystalline product was filtered, washed with dilute HBr, and dried *in vacuo* for 8 hr at room temperature. *Anal.* Calcd for  $Ta_6Br_{15}(H_2O)_3$ : Ta, 45.38; Br, 50.10. Found: Ta, 45.27; Br, 49.88.

**Preparation of  $[(C_2H_5)_4N]_3[(Ta_6Cl_{12})Cl_6]$ .**—A sample of  $Ta_6Cl_{15} \cdot 6H_2O$  dissolved in anhydrous ethanol was filtered into a round-bottom flask and cooled in an ice bath. After addition of an excess of tetraethylammonium chloride ( $(C_2H_5)_4NCl$ ) the solution was flushed thoroughly with argon, saturated with gaseous HCl, and cooled to freezing with liquid nitrogen. The flask then was evacuated and allowed to warm to room temperature. Vacuum distillation of the ethanol left a green powder and the excess of  $(C_2H_5)_4NCl$ , which was removed by washing the product with small portions of ethanol. The green powder was analyzed after drying *in vacuo*. *Anal.* Calcd for  $C_{24}H_{60}N_3Ta_6Cl_{18}$ : Ta, 51.34; Cl, 30.18; C, 13.63; H, 2.86. Found: Ta, 51.39; Cl, 30.16; C, 13.43; H, 3.03.

**Preparation of  $[(C_2H_5)_4N]_2[(Ta_6Cl_{12})Cl_6]$ .**—Chlorine gas was passed through a filtered solution of  $Ta_6Cl_{12}^{2+}$  in anhydrous ethanol. Excess  $(C_2H_5)_4NCl$  was added and the solution was saturated with HCl. A red crystalline product was obtained after evaporation of the solution up to the point of crystallization and then chilling for 1 hr in an ice bath. The product was filtered, dissolved in the minimum volume of DMF (dimethylformamide), and recrystallized by addition of ethanol to the DMF solution. The brilliant red crystals were washed with ethanol and air dried. *Anal.* Calcd for  $C_{16}H_{40}N_2Ta_6Cl_{18}$ : Ta, 54.71; Cl, 32.16; C, 9.68; H, 2.03. Found: Ta, 54.81; Cl, 32.23; C, 9.78; H, 2.04.

**Preparation of  $[(C_6H_5)_4As]_2[(Ta_6Cl_{12})Cl_6]$ .**—This compound was prepared exactly as the above  $(C_2H_5)_4N^+$  salt, except excess tetraphenylarsonium chloride was added to the solution. *Anal.* Calcd for  $C_{48}H_{40}As_2Ta_6Cl_{18}$ : Ta, 43.59; Cl, 25.62; C, 23.15; H, 1.62. Found: Ta, 43.07; Cl, 25.46; C, 22.95; H, 1.62.

**Preparation of  $[(C_2H_5)_4N]_2[(Ta_6Cl_{12})Br_6]$ .**—A filtered solution

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of  $Ta_6Cl_{12}^{2+}$  in anhydrous ethanol was oxidized with ethanolic bromine, excess  $(C_2H_5)_4NBr$  was added, and the solution was saturated with gaseous  $HBr$ . After evaporating to the point of crystallization and chilling in an ice bath, the red crystals were filtered, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd for  $C_{16}H_{40}N_2Ta_6Cl_{12}Br_6$ : Ta, 48.23; C, 8.54; H, 1.79. Found: Ta, 48.4; C, 8.51; H, 2.06. Determination of total halide by titration with  $Ag^+$  gave  $X:Ta = 2.97$ .

**Preparation of  $[(C_2H_5)_4N]_2[(Ta_6Br_{12})Br_6]$ .**—A filtered ethanol solution of  $Ta_6Br_{12}^{2+}$  was oxidized with ethanolic bromine, excess  $(C_2H_5)_4NBr$  was added, and the solution was saturated with gaseous  $HBr$ . After evaporation of most of the solvent the dark red crystals were filtered, washed with ethanol, and dried *in vacuo*. This compound fumed slightly in air and was stored in the dry-box. *Anal.* Calcd for  $C_{16}H_{40}N_2Ta_6Br_{18}$ : Ta, 38.99; Br, 51.65; C, 6.90; H, 1.45. Found: Ta, 38.68; Br, 51.27; C, 6.65; H, 1.50.

**Preparation of  $[(C_2H_5)_4N]_2[(Ta_6Br_{12})Cl_6]$ .**—A filtered solution of  $Ta_6Br_{12}^{2+}$  in ethanol was oxidized with chlorine, excess  $(C_2H_5)_4NCl$  was added, and the solution was saturated with gaseous  $HCl$ . The deep red crystals were isolated as for the previous compound. *Anal.* Calcd for  $C_{16}H_{40}N_2Ta_6Br_{12}Cl_6$ : Ta, 43.12; C, 7.63; H, 1.60. Found: Ta, 43.24; C, 7.12; H, 1.59. A weighed sample treated with aqueous  $Ag^+$  gave 0.2008 g of silver halide, compared with the calculated 0.1966 g.

**Niobium Complexes. Preparation of  $[(Nb_6Cl_{12})Br_2(H_2O)_4] \cdot 3H_2O$ .**—An aqueous solution of  $Nb_6Cl_{14} \cdot 8H_2O$  was trickled through a column of anion-exchange resin (Amberlite IRA-400) in the bromide form. The resulting solution was made *ca.* 0.6 M in  $HBr$  and evaporated slowly at  $30^\circ$  to yield black crystals, which were collected on a frit, washed with ether, and dried *in vacuo*. *Anal.* Calcd for  $Nb_6Cl_{12}Br_2 \cdot 7H_2O$ : Nb, 43.93. Found: Nb, 43.97. A weighed sample when treated with aqueous  $Ag^+$  gave 0.3511 g of silver halide, compared to the calculated 0.3442 g.

**Preparation of  $[(Nb_6Cl_{12})F_2(H_2O)_4] \cdot 4H_2O$ .**—An aqueous solution of  $Nb_6Cl_{14} \cdot 8H_2O$  was made *ca.* 0.6 M in  $HF$  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 filtered, washed with ether, and dried *in vacuo*. *Anal.* Calcd for  $Nb_6Cl_{12}F_2(H_2O)_8$ : Nb, 47.85; Cl, 36.52. Found: Nb, 47.94; Cl, 37.28; Cl:Nb, 2.04.

**Preparation of  $[C_3H_7NH_3]_2[(Nb_6Cl_{12})Cl_6]$ .**—This complex containing the *n*-propylammonium cation was prepared in manner similar to that reported previously for the  $(C_2H_5)_4N^+$  salt.<sup>6</sup> *Anal.* Calcd for  $C_6H_{20}N_2Nb_6Cl_{18}$ : Nb, 42.82; Cl, 49.03; C, 5.54; H, 1.54. Found: Nb, 42.11; Cl, 47.47; C, 5.46; H, 1.85; Cl:Nb, 2.95.

**Preparation of  $[C_3H_7NH_3]_3[(Nb_6Cl_{12})Cl_6]$ .**—This salt also was prepared according to the procedure given previously.<sup>6</sup> However in this case pure oxygen was bubbled through the solution of  $Nb_6Cl_{12}^{2+}$  in ethanol saturated with  $HCl$  for 30 min. When the oxidation to  $Nb_6Cl_{12}^{3+}$  was complete, a 2.5-mol excess of *n*-propylammonium chloride in ethanol was added. The solution was concentrated by vacuum distillation of ethanol, resaturated with  $HCl$ , and allowed to stand overnight. The product was filtered, washed with chloroform, and dried *in vacuo* to a dark olive powder. *Anal.* Calcd for  $C_9H_{30}N_3Nb_6Cl_{18}$ : Nb, 40.52; Cl, 46.39; C, 7.85; H, 2.20. Found: Nb, 40.41; Cl, 46.18; C, 7.51; H, 2.41; Cl:Nb, 2.99.

**Preparation of  $[C_3H_7NH_3]_2[(Nb_6Cl_{12})Br_6]$ .**—A solution of  $(Nb_6Cl_{12})Br_2 \cdot 7H_2O$  in ethanol was saturated with  $HBr$  and oxidized with a solution of bromine in ethanol. After a 6-mol excess of *n*-propylammonium bromide was added, the solution was concentrated to *ca.* one-third its original volume and cooled at  $-25^\circ$  for 1 hr. The product was isolated on a frit as a black powder, washed with copious quantities of chloroform and ether, then dried *in vacuo*. *Anal.* Calcd for  $C_6H_{20}N_2Nb_6Cl_{12}Br_6$ : Nb, 35.23; C, 4.55; H, 1.27. Found: Nb, 34.50; C, 4.92; H, 1.46. Determination of total halogen by titration with  $Ag^+$  gave  $X:Nb = 3.01$ .

**Preparation of  $[C_3H_7NH_3]_2[(Nb_6Br_{12})Br_6]$ .**—This compound was prepared as in the preceding preparation except  $Nb_6Br_{14} \cdot 8H_2O$  was used as starting material. The product was isolated as a brown powder. *Anal.* Calcd for  $C_6H_{20}N_2Nb_6Br_{18}$ : Nb, 26.34; Br, 67.98; C, 3.40; H, 0.95. Found: Nb, 26.43; Br, 67.18; C, 2.97; H, 1.11; Br:Nb = 2.96.

In exactly the same manner a salt containing the tetra-*n*-butylammonium cation was prepared by adding  $(n-C_4H_9)_4NBr$  to the solution rather than  $n-C_3H_7NH_3Br$ . *Anal.* Calcd for  $[(C_4H_9)_4N]_2[(Nb_6Br_{12})Br_6]$ : Nb, 22.47; Br, 57.99; C, 15.48; H, 2.93. Found: Nb, 22.84; Br, 56.87; C, 15.82; H, 2.60; Br:Nb = 2.90.

**Preparation of  $[n-C_3H_7NH_3]_2[(Nb_6Br_{12})Cl_6]$ .**—This preparation was carried out as for the preceding compound, except the initial cluster solution was saturated with  $HCl$  and oxidized by bubbling chlorine into the solution for 45 sec. The product was isolated as fine black crystals, washed with a small volume of ethanol followed by larger volumes of chloroform, and dried *in vacuo*. *Anal.* Calcd for  $C_6H_{20}N_2Nb_6Br_{12}Cl_6$ : Nb, 30.15; C, 3.89; H, 1.09. Found: Nb, 30.98; C, 3.97; H, 1.18. A weighed sample yielded 0.2934 g of silver halide compared to the calculated 0.2998 g.

The corresponding salt containing  $(n-C_4H_9)_4N^+$  was prepared in an exactly analogous manner. *Anal.* Calcd for  $[(n-C_4H_9)_4N]_2[(Nb_6Br_{12})Cl_6]$ : Nb, 25.18; C, 17.35; H, 3.28. Found: Nb, 25.54; C, 17.50; H, 3.50.

**Preparation of  $[(C_2H_5)_4N]_4[(Nb_6Cl_{12})F_6]$ .**—A filtered solution of  $Nb_6Cl_{14} \cdot 8H_2O$  in ethanol was made acidic with a small amount of  $HF$ . To this solution in a Teflon beaker was added a 20-mol excess of  $(C_2H_5)_4NF$ , and the solution evaporated to *ca.* 5% of its original volume with heating. The solution was cooled to  $25^\circ$  to allow more complete crystallization before filtering the product, washing with chloroform and ether, and drying *in vacuo*. This product was recrystallized by dissolving the material in ethanol and repeating the preceding procedure. *Anal.* Calcd for  $C_{20}H_{50}N_4Nb_6Cl_{12}F_6$ : Nb, 34.46; Cl, 26.30; F, 7.05. Found: Nb, 33.66; Cl, 24.95; F, 6.18; Cl:Nb = 1.94; F:Nb = 0.90.

**Preparation of  $Li_4[(Nb_6Cl_{12})Cl_6]$ .**—The method reported previously<sup>8</sup> for preparation of  $K_4[(Nb_6Cl_{12})Cl_6]$  was used to obtain this compound. Two experiments were performed in attempts to establish the composition of this salt. In one experiment anhydrous  $Nb_6Cl_{14}$  was equilibrated with excess  $LiCl$  at *ca.*  $800^\circ$  for 6 days. The product was extracted *in vacuo* with anhydrous ether to remove unreacted  $LiCl$ , dried, and analyzed. *Anal.* Calcd for  $Li_4Nb_6Cl_{18}$ : Nb, 45.57; Cl, 52.16. Found: Nb, 47.40.

Although a chloride analysis by oxidation of the compound in nitric acid using the "H-tube" technique<sup>15</sup> was attempted, it was evident that incomplete oxidation of the niobium to  $Nb_2O_5$  resulted. This difficulty was indicative of the presence of niobium metal and explains the high niobium analysis. In a second experiment a niobium tube was charged with  $NbCl_5$  and excess  $LiCl$ . The tube was then sealed, placed in a fused silica container which was subsequently evacuated, and equilibrated at  $800^\circ$  for 6 days. After removing the mixture from the tube, excess  $LiCl$  was extracted with ether and the product was analyzed. *Anal.* Found: Nb, 45.54; Cl, 50.74; Cl:Nb = 2.92.

**Analytical Procedures.**—Niobium and tantalum were always determined as the oxide  $M_2O_5$  which was produced by ammonia hydrolysis, the "H-tube" method,<sup>15</sup> or oxidation with nitric acid in a tared crucible. Halogens were determined gravimetrically as silver halide or by potentiometric titration with standard silver nitrate after decomposition of the cluster compounds with either nitric acid or aqueous ammonia. When both chlorine and bromine were present the weight of silver halide was compared with that calculated for a specific sample.

## Results and Discussion

All of the compounds reported here can be prepared

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in close to 100% yield. Except where noted all of the compounds are stable to oxidation or hydrolysis in air at room temperature. The notable exceptions are  $\text{H}_2\text{Ta}_6\text{Cl}_{18} \cdot 6\text{H}_2\text{O}$ , which effloresced slowly, and  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[(\text{Ta}_6\text{Br}_{12})\text{Br}_6]$ , which hydrolyzed with liberation of HBr. Apparently the beautiful red, octahedral crystals of  $\text{H}_2\text{Ta}_6\text{Cl}_{18} \cdot 6\text{H}_2\text{O}$  can be preserved only by storing them under the solution from which they crystallized. It is presumed that the water in this compound is associated with hydration of the protons, which according to the stoichiometry are indicated to be present as  $\text{H}_7\text{O}_3^+$ . A structure determination of this compound is in progress in these laboratories.<sup>16</sup>

In no case was it possible to obtain fully anated cluster species from aqueous solutions. Crystallization from aqueous solution, even in the presence of high concentration of hydrogen halide, always provided hydrated compounds of the type  $(\text{M}_6\text{X}_{12})\text{X}_n \cdot m\text{H}_2\text{O}$ . No particular effort was made in this work to determine water of hydration directly, so the hydration number as determined by difference after metal and halogen analyses should be regarded as reliable only within  $\pm 1$  unit.

The stability of the  $\text{M}_6\text{X}_{12}^{n+}$  species toward hydrolytic degradation in aqueous solution decreases in the order  $\text{M} = \text{Ta} > \text{Nb}$ ,  $\text{X} = \text{Cl} > \text{Br}$ , and  $n = 2 > 3 > 4$ . For example, in weakly acidic or neutral solution only the tantalum clusters with  $n = 3$  or 4 were found to be even moderately stable. Also if solutions of either  $\text{Nb}_6\text{Br}_{12}^{2+}$  or  $\text{Ta}_6\text{Br}_{12}^{2+}$  were held at temperatures above *ca.* 50° hydrolysis and precipitation of hydrated metal oxide became a troublesome feature during preparation of the hydrated derivatives. It is possible that the hydrolysis is speeded by air oxidation of the cluster to the 3+ state, which then is more rapidly hydrolyzed. At low pH and elevated temperature conversion of  $\text{Ta}_6\text{Cl}_{12}^{2+}$  to  $\text{Ta}_6\text{Cl}_{12}^{3+}$  by air oxidation is fairly rapid. In fact, if  $\text{M}_6\text{X}_{12}^{2+}$  derivatives completely free of  $\text{M}_6\text{X}_{12}^{3+}$  are desired, the solutions must be carefully protected from oxidation. Spreckelmeyer<sup>11</sup> has shown that  $\text{Ta}_6\text{X}_{12}^{3+}$  can substitute for  $\text{Ta}_6\text{Cl}_{12}^{2+}$  in the crystals of  $\text{Ta}_6\text{X}_{14} \cdot 8\text{H}_2\text{O}$ .

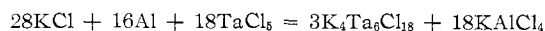
Although direct structural data are available only for  $\text{Ta}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$ ,<sup>13</sup> there is little doubt that these hydrated derivatives have at least some of the water molecules coordinated to the metal atoms of the cluster unit. In a few instances bands characteristic of coordinated water were observed in the infrared spectra.<sup>17</sup> For example the Ta—O stretching frequencies in  $[(\text{Ta}_6\text{Cl}_{12})\text{X}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$  were observed at 404 and 402  $\text{cm}^{-1}$ , respectively, for  $\text{X} = \text{Cl}$  and  $\text{X} = \text{Br}$ . The compound  $[(\text{Ta}_6\text{Br}_{12})\text{Br}_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  exhibited an unusually strong band at 990  $\text{cm}^{-1}$  in addition to bands at 3500

and 1630  $\text{cm}^{-1}$ . The band at 990  $\text{cm}^{-1}$  may be assigned as the  $\text{OH}_2$  rocking vibration of the coordinated water molecule.<sup>18</sup>

In nonaqueous media the 3+ and 4+ oxidation states of the  $\text{M}_6\text{X}_{12}^{n+}$  clusters are much more stable than in water, particularly when they are completely anated. Synthesis of the  $(\text{M}_6\text{X}_{12})\text{Y}_6^{2-}$  derivatives is straightforward. In the alcohols oxidation to the  $\text{M}_6\text{X}_{12}^{4+}$  state is easily attained with chlorine or bromine, and complete anation is ensured by saturating the solutions with the appropriate gaseous hydrogen halide.

The  $\text{M}_6\text{X}_{12}^{3+}$  anionic complexes are more difficult to obtain in a pure state for  $\text{M} = \text{Ta}$  than for  $\text{M} = \text{Nb}$ . The 3+ niobium complexes are easily prepared using oxygen to oxidize  $\text{Nb}_6\text{Cl}_{12}^{2+}$  rapidly; subsequent oxidation to the 4+ state is very slow under these conditions.<sup>6</sup> However, this scheme fails in the tantalum clusters because oxidation to  $\text{Ta}_6\text{X}_{12}^{4+}$  by oxygen is rapid in alcohol-HX solutions. Thus the oxidation state must be carefully adjusted to 3+ before addition of hydrogen halide. Thereafter the solution must be rigorously protected from oxygen.

It was found that in the general case  $(\text{M}_6\text{X}_{12})\text{Y}_6^{4-}$  complexes could not be prepared by the solution method. Particular difficulties resulted from the ease of oxidation of the 2+ clusters and low stability of the anions toward solvation, even in the solvents acetonitrile and dimethyl sulfoxide. In the absence of solvents, however, certain alkali metal salts can be prepared, *viz.*,  $\text{K}_4\text{Nb}_6\text{Cl}_{18}$ <sup>3,19</sup> and the  $\text{Li}_4\text{Nb}_6\text{Cl}_{18}$  described here. An analogous tantalum salt,  $\text{K}_4\text{Ta}_6\text{Cl}_{18}$ , has been prepared from the reaction of KCl,  $\text{TaCl}_5$ , and aluminum in a sealed Vycor tube at 540° for 5 days. The overall reaction proceeds according to



It should be noted that Mackay and Schneider<sup>8</sup> reported the preparation of  $((\text{C}_2\text{H}_5)_4\text{N})_4\text{Nb}_6\text{Cl}_{18}$  by the same solution techniques used to synthesize the 3+ and 4+ cluster complexes. These conditions easily lead to contamination of the desired 2+ complex by oxidation to the corresponding 3+ complex. Indeed, analysis of the spectrum given by these authors<sup>20</sup> for  $((\text{C}_2\text{H}_5)_4\text{N})_4\text{Nb}_6\text{Cl}_{18}$  clearly shows<sup>21</sup> that it corresponds to the spectrum of  $\text{Nb}_6\text{Cl}_{18}^{3-}$ . This illustrates that great precaution must be taken in establishing the oxidation state and purity of these cluster derivatives before further studies are made, especially determination of magnetic susceptibilities and electronic spectra.

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(17) A detailed study of the infrared spectra of  $\text{M}_6\text{X}_{12}$  derivatives has been made, and the results will appear in a subsequent paper in this series.