HEXANUCLEAR CLUSTER COMPLEXES OF

NIOBIUM AND TANTALUM WITH NEUTRAL AND ANIONIC LIGANDS

by

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ABSTRACT

HEXANUCLEAR CLUSTER COMPLEXES OF

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A variety of coordination compounds based on hexanuclear $(M_6X_{12})^{n+}$ central cations were synthesized from hydrated niobium or tantalum halides $[(M_6X_{12})X_2(H_2O)_4] \cdot 4H_2O$ either by replacing water terminal ligands with other neutral ligands L or by replacing halide terminal ligands X with other anionic ligands. Water molecules appear to be difficult to replace by other neutral ligands. Though a number of neutral ligands L were tried, only a few new complexes of the general formula $[(M_6X_{12})X_2L_4]$ could be prepared.

A microscopic method was developed to check if a particular anion will replace halide terminal ligands to form crystalline hydrated $(M_6X_{12})^{n+}$ derivatives. This method showed that halide terminal ligands are easily replaced, and it proved extremely valuable in guiding subsequent full-scale preparations.

A number of well-crystallized hydrated carbonate, oxalate, toluene sulfonate, sulfate, and formate derivatives of $(M_6X_{12})^{n+}$ central cations were synthesized and characterized. Anionic ligands may be selective in their reactions.

They appear to be useful for separating M_6X_{12} cluster cations of different kinds. It was found that the oxalate ion precipitates out $(M_6Br_{12})^{2+}$ cations of niobium and tantalum as solid crystalline $M_6Br_{12}C_2O_4 \cdot 11H_2O$, whereas it does not react with the corresponding chloride cluster cations $(M_6Cl_{12})^{2+}$. Toluene sulfonic acid on the other hand was found to easily precipitate $(Ta_6Br_{12})^{3+}$ cations as $Ta_6Br_{12}(C_7H_7SO_3) \cdot 11H_2O$, whereas it will react with Nb_6Br_{12} cations only under greatly different conditions. Carboxylate anions such as formate and particularly acetate appear to be able to replace bridging halogens of M_6X_{12} cluster cations as evidenced by products with halogen/metal ratios substantially lower than 12/6.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

IV. RESULTS AND DISCUSSION

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Coordination compounds based on metal halide clus-
ters M_6X_{12} of niobium and tantalum as central cations
represent a unique branch of coordination chemistry that has
not been extensively investigated. The $M_6X_{12}{}^{n+}$ cluster
cations consist of internal metal-metal bonded M_6 octahedra
and twelve halogens bridging over the octahedral edges.[1]
Terminal ligands can attach to the vacant site on each metal
atom resulting in negative, neutral, and positive complexes.
These complexes can be prepared with the central cation in
different oxidation states. Examples are:
$\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6\right]^2$, $\left[(Nb_6Cl_{12})Cl_2(C_2H_5CN)_4\right]^3$,
and $\left[(Nb_6Cl_{12})(DMSO)_6\right](ClO_4)_2{}^4$. The structure of an octa-
hedral complex based on the M_6X_{12} central cation is shown in
figure 1.

Coordination compounds of the M_6X_{12} central cation
may be expected to show some interesting features. $(M_6X_{12})^{n+}$
central cations equipped with a mixed set of terminal ligands
can be expected to be distorted due to the greater attraction
between the stronger bonding terminal ligands and the metal
atom they are coordinated to. Indications of the strength
of the MO bonding system in the electron deficient $(M_6X_{12})^{n+}$
cluster unit and of the donor strength of various ligands

● - M

◉ - L

○ - X
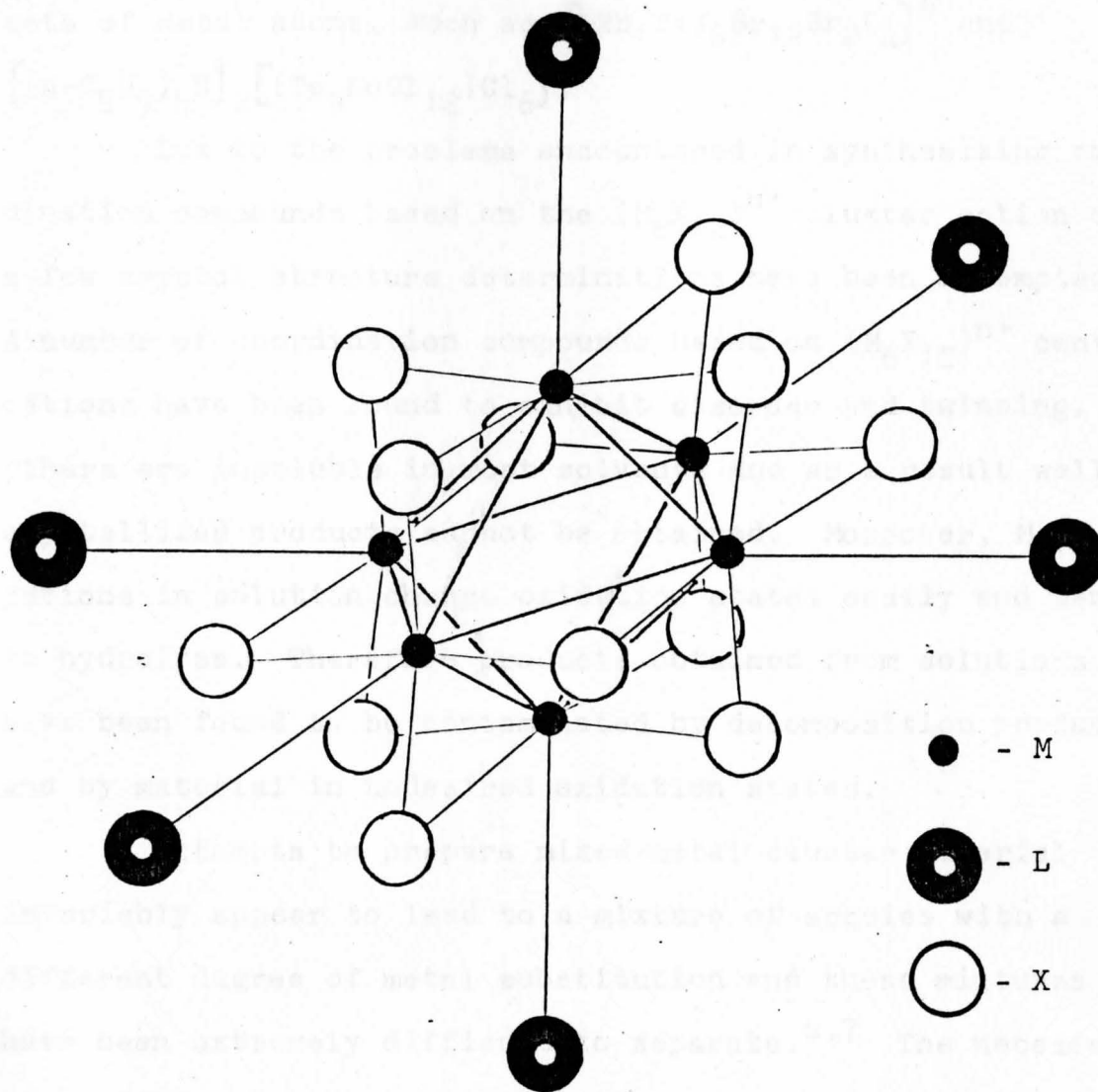
Fig. 1. Octahedral Complex Based on M_6X_{12}
Central Cation.

with respect to the central cation can be determined by
X-ray structure analysis. Additional information may be ob-
tained from distortions of M_6X_{12} octahedra containing mixed
sets of metal atoms, such as $[(Nb,Ta)_6Br_{12}Br_2L_4]^5$ and
$[(n-C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]$.[6]

Due to the problems encountered in synthesizing coor-
dination compounds based on the $(M_6X_{12})^{n+}$ cluster cation only
a few crystal structure determinations have been attempted.
A number of coordination compounds based on $(M_6X_{12})^{n+}$ central
cations have been found to exhibit disorder and twinning.
Others are insoluble in most solvents and as a result well
crystallized products cannot be obtained. Moreover, M_6X_{12}
cations in solution change oxidation states easily and tend
to hydrolyze. Therefore products obtained from solutions
have been found to be contaminated by decomposition products
and by material in undesired oxidation states.

Attempts to prepare mixed-metal cluster material
invariably appear to lead to a mixture of species with a
different degree of metal substitution and these mixtures
have been extremely difficult to separate.[6,7] The necessary
separations might be easy to achieve via well-crystallized
and reasonably inert coordination compounds containing
ligands that selectively complex one particular oxidation
state of the cluster or one particular metal atom.

The purpose of this work was to find which ligands
will form well-crystallized and well-defined complexes with
$(M_6X_{12})^{n+}$ cluster cations and to investigate if there are

ligands that prefer particular oxidation states or bond
preferentially to one metal, e.g. to niobium rather than
tantalum.

CHAPTER II

REVIEW OF PREVIOUS WORK

As early as 1907 Chabrie[8] isolated a small quantity of a dark green substance during the reduction of $TaCl_5$ with gaseous hydrogen. After only one analysis he deduced the formula of the compound to be $TaCl_2 \cdot 2H_2O$. Chapin,[9] by a reduction of $TaBr_5$ with sodium amalgam, prepared a hydrated green tantalum subbromide that analyzed $TaBr_{2.34} \cdot 1.18H_2O$. He found that only one-seventh of the bromine could be precipitated by silver nitrate and determined a molecular weight of 2275 for his compound. From these data he concluded that the substance contained discrete $(Ta_6Br_{12})^{2+}$ units and formulated it correctly as $Ta_6Br_{14} \cdot 7H_2O$.

Following the work by Chabrie and Chapin, Harned[10] carried out investigations to determine whether it was possible to prepare a niobium chloride analog of the compound prepared by Chapin. Using Chabrie's method, he obtained a compound which he formulated as $(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$.

Schäfer and Bauer[11] established the formula for the tantalum chloride as being $Ta_6Cl_{14} \cdot 8H_2O$, instead of $Ta_6Cl_{14} \cdot 7H_2O$, by analytical determination of tantalum, chlorine, water, and the oxidation number of the metal. It is now generally assumed that all of the above mentioned subhalides of niobium and tantalum are octahydrates. Hydrated

halides $M_6X_{14} \cdot 8H_2O$ which serve as the starting materials for the preparation of a number of solid M_6X_{12} derivatives are now easily accessible using a synthesis developed by Koknat, Parsons, and Vongvusharintra.[12]

By means of X-ray diffraction studies on concentrated ethanolic solutions of the hydrates of Nb_6Cl_{14}, Ta_6Cl_{14}, and Ta_6Br_{14}, Pauling and coworkers[1] established the structure of the $(M_6X_{12})^{n+}$ cation as an M_6 octahedron with twelve halogens bridging over the octahedral edges. Further crystallographic proof for the presence of octahedral M_6 groups was obtained by Schäfer's group from crystal determinations of Nb_6Cl_{14}[13] and Ta_6I_{14}.[14]

McCarley, Hughes, Cotton, and Zimmerman[15] in 1965, and Espenson and McCarley[16] in 1966 established that $(M_6X_{12})^{2+}$ cluster cations in solution may undergo one and two electron oxidation, and subsequently a variety of hydrated halides containing M_6X_{12} cations in the oxidation states +3 and +4 were synthesized. Spreckelmeyer and Schäfer[17] reported the isolation of the hydrates $(Ta_6Cl_{12})Cl_3 \cdot 7H_2O$ and $Nb_6Cl_{15} \cdot 7H_2O$. Spreckelmeyer[18] also prepared $Ta_6Br_{15} \cdot 7H_2O$, $Ta_6Br_{16} \cdot 7H_2O$, and $Ta_6Cl_{16} \cdot nH_2O$, and Hughes[19] reported the synthesis of $Ta_6X_{15} \cdot 6H_2O (X = Cl, Br)$.

Since each of the six metal atoms of an M_6X_{12} cation has one site open for attachment of a terminal ligand, the large cluster cations may act as central cations in octahedral complexes, and they share this property with single transition element cations. Thus the M_6X_{14} octahydrates represent

complexes with $(M_6X_{12})^{2+}$ central cations and two halide ions and four water molecules as terminal ligands,[20] and they should be formulated as $[(M_6X_{12})X_2(H_2O)_4] \cdot 4H_2O$.

McCarley's group,[19,21] Mackay and Schneider,[22] Spreckelmeyer,[23] and Schäfer's group[24] prepared anionic halide complexes of the general formula $A_n(M_6X_{12})Y_6$ (A = univalent cation; n = 2,3; M = Ta, Nb; X = Cl, Br; Y = F, Cl, Br, I). Ethanolic solutions of the appropriate hydrates $M_6X_{14} \cdot 8H_2O$ were saturated with hydrogen halide, HY, and after oxidation of the cluster cation the complex was precipitated by the addition of an excess of the halide, AY.

Field and Kepert[25] reported a series of compounds $[(Nb_6Cl_{12})Cl_2L_4]$ with neutral donor ligands L. To obtain the triphenylarsine oxide, triphenylphosphine oxide, and pyridine-N-oxide complexes, ethanolic solutions of $Nb_6Cl_{14} \cdot 8H_2O$ and the particular ligand, L, were mixed, and the resultant mixture was evaporated if necessary. Dimethyl-sulfoxide and dimethylformamide complexes of Nb_6Cl_{14} were obtained by dissolving $Nb_6Cl_{14} \cdot 8H_2O$ in the liquid ligand and precipitating the complex formed with 2-propanol.

Additional complexes reported are $[(Nb_6Cl_{12})Cl_2(C_2H_5CN)_4]$, synthesized by Parsons[3], and $[(Nb_6Cl_{12})Cl_2(CH_3CN)_4]$, $[(Nb_6Br_{12})Br_2(CH_3CN)_4]$, and $[(Nb_6Cl_{12})F_2(C_5H_5NO)_4]$, all prepared by Vongvusharintra.[26]

Electronic spectra of compounds containing M_6X_{12} cations were reported in a number of papers. However, early measurements often contained errors, apparently caused by

the oxidation of the M_6X_{12} species in the solution to be measured.[27] Tabulations of reliable spectral data are given by Mackay and Schneider,[28] Fleming and McCarley,[29] and by Spreckelmeyer.[30] Of these tabulations, the one by Spreckelmeyer is by far the most extensive and complete. It must be pointed out, however, that even Spreckelmeyer's tabulations do not contain all M_6X_{12} cations in all of the known oxidation states.

For a particular $(M_6X_{12})^{n+}$ cluster cation, the spectrum varies with the oxidation state. Therefore, spectral data may be used to determine the oxidation state of an M_6X_{12} cation in a particular substance.

An indication of the oxidation state of an M_6X_{12} cation may also be obtained from the color exhibited in solution or in the solid state. Table 1 lists colors shown by different $(M_6X_{12})^{n+}$ cations.

TABLE 1

COLORS OF M_6X_{12} CENTRAL CATIONS

M_6X_{12} Cation	In Solution	In the Solid State
$(Nb_6Cl_{12})^{2+}$	brownish green[a]	dark brown[a]
$(Nb_6Cl_{12})^{3+}$	reddish brown[b]	brown[b]
$(Nb_6Cl_{12})^{4+}$	dark yellowish brown[c]	black[b]
$(Nb_6Br_{12})^{2+}$	brownish green[a]	dark brown[a]
$(Nb_6Br_{12})^{3+}$	[e]	[e]
$(Nb_6Br_{12})^{4+}$	red-violet[c]	
$(Ta_6Cl_{12})^{2+}$	emerald green[a]	dark emerald green[a]
$(Ta_6Cl_{12})^{3+}$	brownish yellow[d]	brown[a]
$(Ta_6Cl_{12})^{4+}$	red[c]	red[a]
$(Ta_6Br_{12})^{2+}$	dark emerald green[a]	emerald green[a]
$(Ta_6Br_{12})^{3+}$	brownish yellow[d]	brown[a]
$(Ta_6Br_{12})^{4+}$	red[c]	red[a]

[a]B. Spreckelmeyer, Z. Anorg. Allg. Chem., 358, 147 (1968)

[b]F. W. Koknat, personal communication.

[c]B. Spreckelmeyer, Z. Anorg. Allg. Chem., 368, 18 (1969)

[d]B. Spreckelmeyer and H. Schäfer, J. Less-Common Metals, 13, 127 (1967).

[e]no colors reported so far

CHAPTER III

EXPERIMENTAL

Equipment and Materials

The moisture sensitive niobium and tantalum penta-
halides were handled on a vacuum line or in a nitrogen atmos-
phere dry box. Nitrogen gas was dried by passing it over
Linde 4A molecular sieves, and in the dry box the nitrogen
atmosphere was kept moisture free by an adequate supply of
exposed phosphorus pentoxide. Reactions involving moisture
sensitive compounds were carried out in sealed, evacuated
Vycor glass tubes which were heated in a manually controlled
Lindberg hinged split tube furnace.

Tantalum and niobium pentahalides were purchased
from Research Organic/Inorganic Corporation and used without
further purification. Niobium metal (E.I. du Pont de Nemours
and Co.) was used in the form of pellets of approximately
1 mm diameter; tantalum metal (Research Organic/Inorganic
Corp.) as a 325-mesh powder. These materials were stored in
a dry box under nitrogen. 1,2,6-trimethyl-4-pyridone, used
as a possible ligand in reactions, was obtained from D.
Teminsky, an undergraduate student at Youngstown State Uni-
versity. The cluster compound, Mo_6Cl_{12} which was used as a
starting material, was obtained from T. Adaway, an under-
graduate student at Youngstown State University.

Analytical Procedures

Niobium and tantalum were determined gravimetrically as the oxides Nb_2O_5 and Ta_2O_5. Weighed samples were placed into tared crucibles, decomposed by concentrated ammonium hydroxide, thereafter by nitric acid, slowly evaporated to dryness, and then ignited.

For compounds containing sulfate or toluene sulfonate a different approach was necessary. Each sample was treated with 30% hydrogen peroxide and then heated on the lowest setting of a hot plate. Later an equal volume of concentrated ammonium hydroxide was added to break up the complex. The solution was then acidified to a pH value of about 4 and heated to rid the solution of excess peroxide. The precipitated oxide was filtered and thereafter ignited in a tared crucible.

The halogens were determined potentiometrically by titrating against a standard silver nitrate solution. The sample was dissolved in water and decomposed by adding sodium hydroxide pellets. The solution was acidified by nitric acid and titrated versus the silver nitrate solution.

The carbon, hydrogen, and nitrogen analyses were done by M-H-W Laboratories, Analytical Division, Garden City, Michigan.

Physical Measurements

Visible, ultraviolet, and infrared absorption spectra for solid samples were obtained using a Cary Model 14 recording spectrophotometer. The samples were ground in a mortar, mixed with mineral oil, and pressed between two quartz plates. All spectral data in this work will be given in the units kilokaiser (kK), since this is the unit that was used by Spreckelmeyer in his comprehensive tabulations of spectra.

X-ray powder patterns were taken using a 57.3 mm diameter Debye-Scherrer powder camera. Finely powdered samples were packed and hermetically sealed in 0.2 mm diameter Lindemann glass capillaries and exposed to Ni-filtered Cu radiation. Exposure times varied from fifteen to twenty-four hours.

Synthesis

Starting Materials

Hydrated Hexanuclear Halides $M_6X_{14} \cdot 8H_2O$

Hydrated hexanuclear halides $M_6X_{14} \cdot 8H_2O$ that were needed as starting materials were prepared by a method described by Koknat, Parsons, and Vongvusharintra.[12] In a dry box weighed amounts of niobium or tantalum metal M, its pentahalide MX_5, and of an alkali halide AX were intimately mixed by grinding in a mortar and then transferred into

Vycor reaction tubes. The reaction tubes were then sealed on the vacuum line and heated in a manually controlled Lindberg split tube furnace. The solid halide $A_4M_6X_{18}$ was formed according to the following equation.

$$20AX + 14MX_5 + 16M \longrightarrow 5A_4M_6X_{18} \qquad (1)$$
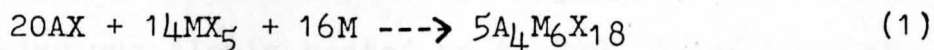
The solid halide was dissolved in distilled water, and from the filtered solution the hydrated halide $M_6X_{14} \cdot 8H_2O$ was precipitated using the appropriate concentrated hydrohalic acid HX. The solid hydrate was filtered over a sintered glass filter, washed with water, concentrated hydrohalic acid HX, then with ether, and dried _in vacuo_ over phosphorus pentoxide.

$Nb_6Cl_{14} \cdot 8H_2O$ via $Na_4Nb_6Cl_{18}$
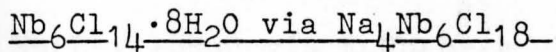
An intimate mixture of 11.7 g (0.200 mol) of sodium chloride, 37.8 g (0.140 mol) of niobium pentachloride, and 60.0 g (0.650 mol) of niobium pellets were slowly heated in a Vycor tube for eleven hours, and thereafter maintained at a temperature of 820° C overnight. The solid $Na_4Nb_6Cl_{18}$ was extracted five times with 1500 ml portions of distilled water. These filtered solutions were heated with equal volumes of concentrated hydrochloric acid. The crystalline product obtained was washed, filtered over a frit, and dried. Yield: 51.0 g = 84.8%.

$Ta_6Cl_{14} \cdot 8H_2O$ via $Na_4Ta_6Cl_{18}$

Using the procedure described above, a mixture
of 25.0 g (70 mmol) of tantalum pentachloride, 5.84 g
(100 mmol) of sodium chloride, and 58.0 g (320 mmol) of
tantalum powder was slowly heated up to 720° C and kept at
this temperature in a Vycor tube for two days. After extract-
ing the obtained $Na_4Ta_6Cl_{18}$ five times with 1500 ml of dis-
tilled water, solid $Ta_6Cl_{14} \cdot 8H_2O$ was precipitated by treating
the dark green solution with an equal volume of concentrated
hydrochloric acid. The product was filtered, washed, and
dried.

Yield: 34.9 g = 81.1%.

$Nb_6Br_{14} \cdot 8H_2O$ via $K_4Nb_6Br_{18}$

A mixture of 13.8 g (29 mmol) of niobium bromide,
4.76 g (40 mmol) of potassium bromide, and 15.0 g (160 mmol)
of niobium pellets was reacted in a Vycor tube at 740° C.
The reaction product was extracted five times with 300 ml
portions of distilled water, and $Nb_6Br_{14} \cdot 8H_2O$ was precipitated
by treating the solution with an equal volume of concentrated
hydrobromic acid.

Yield: 16.0 g = 87.6%

$Ta_6Br_{14} \cdot 8H_2O$ via $K_4Ta_6Br_{18}$

By a similar procedure an intimate mixture of 16.25 g (28 mmol) of tantalum pentabromide, 4.76 g (40. mmol) of potassium bromide, and 28.1 g (100. mmol) of tantalum powder was reacted in a Vycor tube at 720° C. After extracting the $K_4Ta_6Br_{18}$ five times with 1500 ml portions of distilled water, the resulting solution, under moderate heat, was treated with equal volumes of concentrated hydrobromic acid. The final product was filtered, washed, and dried. Yield: 19.1 g = 81.0%.

Synthesis of 1,2,6-Trimethyl-4-Pyridone

This organic compound was used as a ligand because of its structural similarities with pyridine-1-oxide. A method described by D. Cook[31] and modified by J. A. Reeder[32] was employed for its synthesis.

A 16.88 g (100.0 mmol) sample of dehydroacetic acid was dissolved into 75 ml of 40% methylamine, and this solution was heated on a steam bath. After thirty minutes a yellowish liquid was obtained and bubbles were given off. The solution was taken off the bath, and upon cooling white needles of product formed. It was washed with cold water, filtered, and transferred to a vacuum desiccator where it was dried overnight over phosphorus pentoxide. Yield: 12.31 g = 72.4%.

Reactions of Hydrated Halides $M_6X_{14} \cdot 8H_2O$ With Neutral Ligands

Preparation of $[(Ta_6Cl_{12})Cl_2(CH_3CN)_4]$

To a filtered solution of 9.18 g (5.32 mmol) of $Ta_6Cl_{14} \cdot 8H_2O$ in 100 ml of methanol was added 100 ml of acetonitrile, and the resulting solution was heated with stirring. When the volume of the solution reached 150 ml the contents of the reaction vessel were filtered to remove any decomposition material. When, upon continued heating, the volume of the solution had gone down to 40 ml, bumping occurred and shiny dark green crystals formed. Heating was stopped and 100 ml of methanol was added before the product was filtered. The crystals were washed three times with 30 ml of methanol and dried in vacuo over phosphorus pentoxide.

Yield: 3.78 g = 40.6%.

Analysis: Found: Ta, 62.13%; Cl, 28.37%; Cl/Ta, 14.00/6.
Calculated for $[(Ta_6Cl_{12})Cl_2(CH_3CN)_4]$: Ta, 62.17%; Cl, 28.42%.

Preparation of $[(Ta_6Br_{12})Br_2(CH_3CN)_4]$

To a filtered solution of 4.65 g (1.98 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ in 100 ml of methanol was added 100 ml of acetonitrile. The solution was heated with stirring until a volume of 75 ml was attained. At this volume bumping occurred and a black shiny precipitate was seen. Heating was

discontinued and another 100 ml of methanol was added. Stirring was stopped and the precipitate was filtered, washed three times with 30 ml of methanol, and dried in vacuo over phosphorus pentoxide.

Yield: 3.57 g = 75.9%.

Analysis: Found: Ta, 45.63%; Br, 46.98%; N, 2.18%; Br/Ta, 13.96/6.

Calculated for $[(Ta_6Br_{12})Br_2(CH_3CN)_4]$: Ta, 45.84%; Br, 47.32%.

Preparation of $[(Nb_6Cl_{12})Cl_2(C_8H_{11}ON)_4]$

To a filtered solution of 1.28 g (1.07 mmol) of $Nb_6Cl_{14} \cdot 8H_2O$ in 100 ml of methanol was added a 0.51 g (3.70 mmol) sample of 1,2,6-trimethyl-4-pyridone dissolved in 100 ml of absolute ethanol. When almost all of the ligand was added and the total volume of the solution had gone down to 50 ml, a shiny brown precipitate was formed. The product was filtered, washed three times with 10 ml of ethanol, and dried in vacuo over phosphorus pentoxide.

Yield: 0.665 g = 38.7%

Analysis: Found: Nb, 34.42%; Cl, 30.57%; Cl/Nb, 13.97/6.00. Calculated for $[(Nb_6Cl_{12})Cl_2(C_8H_{11}NO)_4]$: Nb, 34.78%; Cl, 30.97%.

In a second attempt a modified method was used that led to a different product. A 1.19 g (1.00 mmol) sample of $Nb_6Cl_{14} \cdot 8H_2O$ was dissolved in 125 ml of methanol and filtered. As this filtrate was heated and stirred a solution

of 0.553 g (4.03 mmol) of 1,2,6-trimethyl-4-pyridone
dissolved in 15 ml of ethanol was added. When the total
volume was 100 ml, a shiny fine-crystalline precipitate was
seen. This greenish-brown product was filtered, washed
three times with 15 ml of ethanol and three times with 50 ml
of acetone, and dried in vacuo over phosphorus pentoxide.
Yield: 0.285 g.

Analysis: Found: Cl, 28.95%.

The analysis showed that a different product was obtained.
No further attempt was made to characterize it.

Preparation of $[(Ta_6Cl_{12})Cl_2(C_8H_{11}NO)_4]$

A 1.74 g (1.00 mmol) sample of $Ta_6Cl_{14} \cdot 8H_2O$ was
dissolved in 100 ml of methanol and filtered. Then 0.548 g
(4.00 mmol) of 1,2,6-trimethyl-4-pyridone were dissolved in
100 ml of ethanol and added dropwise to the tantalum chloride
solution which was heated near boiling. Half way through
the addition there appeared dark, shiny green crystals. The
product was filtered, washed three times with 15 ml of
ethanol, and dried in vacuo over phosphorus pentoxide.
Yield: 0.88 g = 40.9%.

Analysis: Found: Ta, 50.37%; Cl, 22.97%; Cl/Ta, 13.97/6.
Calculated for $[(Ta_6Cl_{12})Cl_2(C_8H_{11}NO)_4]$: Ta, 50.95%;
Cl, 23.29%.

In another attempt the product which was obtained
decomposed violently when exposed to the air after the

drying phase of the synthesis. In this particular reaction
the ratio of tantalum chloride to ligand was somewhat higher
than in the other synthesis. No further analysis was
possible.

Preparation of $[(Mo_6Cl_8)Cl_4(C_8H_{11}NO)_2]$

A 1.03 g (1.00 mmol) sample of Mo_6Cl_{12} was dissolved
in 100 ml of ethanol and filtered. As this filtrate was
heated and stirred 0.548 g (4.00 mmol) of 1,2,6-trimethyl-4-
pyridone dissolved in 100 ml of ethanol was added. Imme-
diately, some fine yellow crystals formed. After all the
ligand had been added heat was applied for ten more minutes,
and then the reaction mixture was set aside to cool. The
precipitate was filtered over a frit, washed three times
with 100 ml of ethanol, and dried in vacuo over phosphorus
pentoxide.

Yield: 1.23 g = 96.4%.

Analysis: Found: Mo, 43.82%; Cl, 31.48%; Cl/Mo, 11.67/6.00.
C, 15.39%; H, 1.25%; N, 2.00%.

Calculated for $[(Mo_6Cl_8)Cl_4(C_8H_{11}NO)_2]$: Mo, 45.12%; Cl,
33.36%; C, 13.07%; H, 1.74%; N, 2.32%.

The low molybdenum and chlorine values may be due to ethanol
present in the product.

Attempt to Prepare a 1,2,6-Trimethyl-4-Pyridone Adduct of
Nb_6Br_{14}—

A 1.82 g (1.00 mmol) sample of $Nb_6Br_{14} \cdot 8H_2O$ was
dissolved in 175 ml of methanol. The filtered solution was
added with heating to 0.552 g (4.00 mmol) of solid 1,2,6-
trimethyl-4-pyridone. No precipitate was formed even though
the solution was taken down to 10 ml. Therefore, another
4 mmol of ligand dissolved in 25 ml of methanol was added.
The solution was again taken down to 50 ml, however, again
no solid product was formed. When the solution was allowed
to evaporate to dryness the solid which resulted was identi-
fied as recrystallized starting material.

In a second attempt 1.82 g (1.00 mmol) of
$Nb_6Br_{14} \cdot 8H_2O$ was dissolved in 100 ml of methanol and filtered.
Into this filtrate was added with heating 0.547 g (4.00 mmol)
of 1,2,6-trimethyl-4-pyridone dissolved in 100 ml of ethanol.
As the addition proceeded a light brown precipitate was ob-
served, and the solution was evaporated to 50 ml. Anhydrous
ether was added (25 ml) and the precipitation increased. The
product was filtered, washed three times with 50 ml of ether
and dried in vacuo for 30 minutes over phosphorus pentoxide.
The filtrate was retreated with ether and more product was
obtained. This retreatment was done four times and finally
the filtrate gave no more product when treated with ether
the sixth time.

Yield: 1.99 g = 89.6% (all five batches).

Analysis: Found: Nb, 20.54%; Br, 42.58%; Br/Nb, 14.46/6.00.

Calculated for $[(Nb_6Br_{12})Br_2(C_8H_{11}NO)_4]$: Nb, 25.05%; Br, 50.28%.

These data show that the compound sought was not obtained.

Attempt to Prepare a 1,2,6-Trimethyl-4-Pyridone Adduct of Ta_6Br_{14}

A 2.36 g (1.00 mmol) sample of $Ta_6Br_{14} \cdot 8H_2O$ was dissolved in 100 ml of methanol and filtered. Into this filtrate was added with heating 0.55 g (4.00 mmol) of 1,2,6-trimethyl-4-pyridone dissolved in 100 ml of ethanol. When the total volume of the solution decreased to 20 ml, a light brown precipitate formed. The product was filtered, washed with 15 ml of methanol and 15 ml of anhydrous ether, and dried in vacuo over phosphorous pentoxide.

Yield: 1.84 g = 70.7%.

Analysis: Found: Ta, 34.44%; Br, 31.78%; Br/Ta, 12.67/6.00.
Calculated for $[(Ta_6Br_{12})Br_2(C_8H_{11}NO)_4]$: Ta, 39.43%; Br, 40.63%.

These data show that the compound sought was not obtained.

Attempt to Prepare a 2,6-Dimethyl-4-Pyrone Adduct of Nb_6Cl_{14}

A 1.21 g (1.00 mmol) sample of $Nb_6Cl_{14} \cdot 8H_2O$ was dissolved in 100 ml of methanol and filtered. As it was heating a solution of 0.496 g (4.00 mmol) of 2,6-dimethyl-4-pyrone in 100 ml of ethanol was added dropwise. Since no

reaction occurred as the volume of solution reached 50 ml, another 4 mmol of the pyrone dissolved in 100 ml of ethanol was added. Again the solution was taken down to 50 ml with no reaction. Therefore, it was allowed to evaporate over-night. When the dark brown solid residue was extracted with chloroform to remove the unreacted pyrone, the resulting solution was found to have a dark brown color, indicating that a sizeable quantity of the desired product had also dissolved. X-ray patterns of the remaining residue did not conclusively show that a new cluster compound had been formed.

In the second attempt 1.21 g (1.00 mmol) of $Nb_6Cl_{14} \cdot 8H_2O$ was dissolved in 100 ml of methanol and filtered. While the filtrate was heated and stirred, 0.992 g (8.00 mmol) of 2,6-dimethyl-4-pyrone dissolved in ethanol was added dropwise. No reaction occurred and the solution was allowed to evaporate to dryness at room temperature. Brown, shiny crystals were seen and this time benzene was used to extract the excess 2,6-dimethyl-4-pyrone. The remaining product was filtered, washed with 15 ml of benzene and 15 ml of ether, and dried in vacuo over phosphorus pentoxide.

Yield: 0.26 g.

Analysis: Found: Nb, 35.43%; Cl, 24.72%; Cl/Nb, 10.98/6.00. Calculated for $[(Nb_6Cl_{12})Cl_2(C_7H_8O_2)_4]$: Nb, 35.95%; Cl, 32.02%.

These data show that the compound sought was not obtained.

Attempt to Prepare a p-Aminophenol Adduct of Nb_6Cl_{14}

To a filtered, heated solution of 1.21 g (1.00 mmol) of $Nb_6Cl_{14} \cdot 8H_2O$ in 100 ml of methanol was added dropwise a solution of 0.50 g (4.6 mmol) p-aminophenol in 100 ml of methanol. No product was formed as the solution was evaporated to 50 ml. After the remaining solvent was allowed to evaporate at room temperature, a black solid residue was observed. The excess of p-aminophenol was removed by extracting with isopropanol. The remaining solid was filtered, washed with 15 ml of ether, and dried in vacuo over phosphorus pentoxide.

Yield: 0.072 g.

No analysis was made since so little product was synthesized.

Attempt to Prepare a Benzophenone Adduct of Nb_6Cl_{14}

To a filtered solution of 1.21 g (1.00 mmol) of $Nb_6Cl_{14} \cdot 8H_2O$ in 100 ml of methanol was added dropwise while heating and stirring 0.77 g (4.0 mmol) of benzophenone dissolved in 100 ml of ethanol. No reaction was observed, even as the volume of the solution was evaporated to 50 ml. Therefore another 0.77 g quantity of benzophenone in 100 ml ethanol was added. Again no reaction was observed as the solution was boiled down to 50 ml. Therefore the remaining solution was allowed to evaporate to dryness at room temperature. From the shiny dark brown residue that was obtained benzophenone was extracted with three 100 ml portions of

chloroform. The remaining solid was filtered over a frit, washed with chloroform, and dried <u>in vacuo</u> over phosphorus pentoxide.

Yield: 0.85 g.

<u>Analysis</u>: Found: Cl, 39.38%.

Calculated for $[(Nb_6Cl_{12})Cl_2(C_{13}H_{10}O)_4]$: Nb, 31.27%; Cl, 27.84%.

Since the Cl value is so close to the value for $Nb_6Cl_{14} \cdot 8H_2O$, it is likely that the product obtained was un-reacted starting material. An X-ray pattern did not exhibit sharp lines, but appeared to be similar to that of $Nb_6Cl_{14} \cdot 8H_2O$.

<u>Attempt to Prepare a Urea Adduct of Nb_6Cl_{14}</u>

A 1.24 g (1.00 mmol) sample of $Nb_6Cl_{14} \cdot 8H_2O$ was dissolved in 100 ml of methanol and filtered. As this solu-tion was heated a solution of 0.24 g (4.00 mmol) of urea dissolved in 100 ml of ethanol was added dropwise. No reac-tion was noted as all the ligand was added and the solution was evaporated down to 50 ml. Another 4 mmol of urea was added, and again no reaction was seen as the volume was again evaporated to 50 ml. The solution was allowed to evaporate to dryness, and after fifteen hours 2.17 g (36.0 mmol) of urea dissolved in 100 ml of ethanol was added with heating and stirring. No bumping occurred and no precipitate was obtained.

Preliminary Experiments Involving Anionic Ligands

Preliminary experiments were performed on a microscopic scale to determine if solid, crystalline products could be obtained from reactions of the hydrates $M_6X_{14} \cdot 8H_2O$ with anionic ligands. In a typical experiment, 10 drops of a 5M solution of $Ta_6Br_{14} \cdot 8H_2O$ in 50% methanol were added to 20 mg of solid ammonium oxalate on a 40 mm diameter porcelain dish. The ensuing formation of flat, green, plate shaped crystals was observed under a Bausch and Lomb Stereozoom microscope.

$Nb_6Br_{14} \cdot 8H_2O$ and Ammonium Oxalate

There appeared very dark green crystals. They had the appearance of flat plates and there was no evidence of unreacted starting material.

$Ta_6Br_{14} \cdot 8H_2O$ and Ammonium Carbonate

Dark green hexagonal crystals were formed. The product was found to be insoluble in water and very slightly soluble in methanol. The color indicates that the material is not oxidized.

$Nb_6Br_{14} \cdot 8H_2O$ and Ammonium Carbonate

Green, very fine crystals were formed. There was no evidence of any unreacted starting material.

$Ta_6Br_{14} \cdot 8H_2O$ and p-Toluenesulfonic Acid

Yellow-brown plates were formed which were insoluble in distilled water and soluble in methanol.

$Nb_6Br_{14} \cdot 8H_2O$ and p-Toluenesulfonic Acid

Some dark brown crystals formed readily but there was also unreacted p-toluenesulfonic acid present in the crucible. The reaction was not complete.

$Ta_6Br_{14} \cdot 8H_2O$ and Ammonium Sulfate

Long rectangular emerald green plates were formed that were insoluble in ethanol. The product was slightly soluble in water and in methanol but it seemed to decompose in these solutions.

$Ta_6Br_{14} \cdot 8H_2O$ and Sodium Formate

Tiny green rectangular plates formed which were insoluble in methanol and distilled water.

$Nb_6Br_{14} \cdot 8H_2O$ and Sodium Formate

Very dark, green crystals formed that were fine in texture. They were insoluble in distilled water and anhydrous ether.

$Ta_6Br_{14} \cdot 8H_2O$ and Ammonium Acetate

At the side of the dish glittering brown octahedra were seen which were insoluble in water, insoluble or slightly soluble in methanol.

In the middle of the dish there appeared an emerald green material. It was water soluble but also contained water insoluble octahedral shaped crystals; the emerald green material was also soluble in methanol.

In addition, in the middle of the dish there was white material that was only somewhat soluble in water.

$Nb_6Br_{14} \cdot 8H_2O$ and Ammonium Acetate

The solid material in the dish was the unreacted starting material. The only other solid that did form was a decomposition product of the cluster hydrate.

$Ta_6Br_{14} \cdot 8H_2O$ and Sodium Nitrite

Very small crystals were formed that were insoluble in water and appeared to be insoluble in methanol. The green color of the product indicated that unoxidized $(Ta_6Br_{12})^{2+}$ cations were present.

$Nb_6Br_{14} \cdot 8H_2O$ and Sodium Nitrite

Very fine, dark crystals appeared on the side of the dish. The material in the center of the dish was different in shape than the solid along the side of the dish.

$Ta_6Br_{14} \cdot 8H_2O$ and Potassium Cyanate

Green and brown substances were formed. The green material was water soluble, somewhat soluble in methanol, and insoluble in ethanol. The brown substance was insoluble in water, soluble in methanol and ethanol. Both the green and brown substances were soluble in acetone.

$Nb_6Br_{14} \cdot 8H_2O$ and Potassium Cyanate

Very fine, green crystals were formed but the large portion of solid in the center of the dish represented un-reacted starting materials.

$Ta_6Br_{14} \cdot 8H_2O$ and Ammonium Thiocyanate

Brown hexagonal plates were formed which were insol-uble in distilled water but very soluble in methanol and ethanol.

$Nb_6Br_{14} \cdot 8H_2O$ and Ammonium Thiocyanate

Two different products were formed together, dark green needles and light brown, fine crystals.

$Ta_6Br_{14} \cdot 8H_2O$ and the Disodium Salt Monohydrate of Iminodiacetic Acid

Very dark, emerald green hexagonal plates were formed. They were insoluble in distilled water, slightly soluble (with decomposition) in methanol, and insoluble in ethanol and acetone.

$Nb_6Br_{14} \cdot 8H_2O$ and the Disodium Salt Monohydrate of Iminodiacetic Acid

Very fine, dark green needle-like crystals were formed. There also appeared some unreacted starting materials.

Reactions of Hydrated Halides $M_6X_{14} \cdot nH_2O$ With Anionic Ligands

Preparation of $(Ta_6Br_{12})C_2O_4 \cdot 11H_2O$

The formation of a crystalline precipitate upon addition of oxalate to an aqueous solution of Ta_6Br_{14} was described before,[33] but no compound had been isolated and characterized.

To a filtered solution of 2.35 g (1.00 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ in 120 ml of distilled water and 20 ml of methanol was slowly added a solution of 1.42 g (10.0 mmol) of ammonium oxalate monohydrate in 100 ml of water. Immediately, a dark glittering precipitate consisting of flat green

plates was formed. The solid product was filtered through a frit, washed four times with 75 ml portions of distilled water, and dried in vacuo over phosphorus pentoxide.

Yield: 1.94 g = 83.2%.

Analysis: Found: Ta, 46.83%; Br, 41.13%; C, 1.22%; H, 0.70%; O(by difference), 10.12%; Br/Ta, 11.93/6.00.

Calculated for $Ta_6Br_{14}C_2O_4 \cdot 11H_2O$: Ta, 46.58%; Br, 41.14%; C, 1.03%; H, 0.95%; O, 10.30%.

Preparation of $Nb_6Br_{12}C_2O_4 \cdot 11H_2O$

A 1.79 g (1.00 mmol) sample of $Nb_6Br_{14} \cdot 8H_2O$ was dissolved in 20 ml of methanol and 80 ml of distilled water. To the filtered solution was added a 1.59 g (11.2 mmol) sample of ammonium oxalate dissolved in 100 ml of distilled water. As soon as the ligand was added shiny, very dark brown crystals were formed. The precipitate was filtered, washed five times with 50 ml of distilled water, and dried in vacuo over phosphorus pentoxide.

Yield: 1.27 g = 80.7%.

Analysis: Found: Nb, 31.14%; Br, 52.78%; C, 1.61%; H, 0.74%; Br/Nb, 11.82/6.00.

Calculated for $Nb_6Br_{12}C_2O_4 \cdot 11H_2O$: Nb, 30.93%; Br, 53.20%; C, 1.33%; H, 1.23%.

Attempt to Prepare an Oxalate Complex of the $(Ta_6Cl_{12})^{2+}$ Cation

A 1.69 g (0.98 mmol) sample of $Ta_6Cl_{14} \cdot 8H_2O$ was dissolved in 20 ml of methanol and 80 ml of distilled water. A 1.62 g (11.4 mmol) sample of ammonium oxalate dissolved in 100 ml of distilled water was added to the filtered cluster solution 10 ml at a time. Heat was applied and no appreciable reaction was observed. After three hours of heating no crystalline solid was obtained, but decomposed by-products were seen in the reaction beaker.

Attempt to Prepare an Oxalate Complex of the $(Nb_6Cl_{12})^{2+}$ Cation

To a filtered solution of 0.24 g (0.20 mmol) of $Nb_6Cl_{14} \cdot 8H_2O$ in 20 ml of methanol and 30 ml of distilled water was added a solution of 0.28 g (2.0 mmol) of ammonium oxalate monohydrate in 50 ml of distilled water. No precipitation occurred. After adding a few milligrams of stannous chloride to prevent oxidation of the $(Nb_6Cl_{12})^{2+}$ ion, the solution was placed on a hot plate and evaporated with stirring to a volume of 15 ml. No solid product precipitated.

Reaction of $Ta_6Br_{14} \cdot 8H_2O$ with Ammonium Carbonate

A 2.37 g (1.00 mmol) sample of $Ta_6Br_{14} \cdot 8H_2O$ was dissolved in 100 ml of methanol and 100 ml of distilled water. This solution was filtered and added dropwise to a 0.99 g (8.7 mmol) sample of ammonium carbonate dissolved in

200 ml of distilled water. As the cluster material was
added there appeared green, very fine crystals. They were
filtered, washed three times with 50 ml of distilled water,
and dried in vacuo over phosphorus pentoxide.

Yield: 1.76 g = 83.1%.

Analysis: Found: Ta, 48.95%; Br, 42.54%; Br/Ta, 11.81/6.00.
Calculated for $Ta_6Br_{12}CO_3 \cdot 8H_2O$: Ta, 48.28%; Br, 42.64%.

Reaction of $Nb_6Br_{14} \cdot 8H_2O$ with Ammonium Carbonate

A 1.82 g (1.00 mmol) sample of $Nb_6Br_{14} \cdot 8H_2O$ was
dissolved in 100 ml of distilled water and filtered. This
solution was added dropwise to a 0.97 g (10.0 mmol) sample
of ammonium carbonate dissolved in 200 ml of distilled water.
The precipitate which formed was very fine in texture and
olive-green in color. The product was filtered, washed
three times with 50 ml of distilled water, and dried in
vacuo over phosphorus pentoxide.

Yield: 0.827 g = 52.4%.

In the second attempt of this synthesis, 1.84 g
(1.01 mmol) of $Nb_6Br_{14} \cdot 8H_2O$ was dissolved in 75 ml of dis-
tilled water and filtered. To this filtrate was added
0.97 g (10.0 mmol) of solid ammonium carbonate. Immediately,
a solid product was formed. The light brown crystals were
filtered, washed three times with 50 ml of distilled water,
and dried in vacuo over phosphorus pentoxide.

Yield: 1.48 g = 93.1%.

Analysis: (of the second batch) Found: Nb, 33.82%; Br, 58.29%; Br/Nb, 12.09/6.00.

Calculated for $Nb_6Br_{12}CO_3 \cdot 4H_2O$: Nb, 33.82%; Br, 58.17%.

The amount of solvent and the yield are the main differences between the two attempts.

Preparation of $Ta_6Br_{12}(C_7H_7SO_3)_3 \cdot 11H_2O$

A 2.38 g (1.00 mmol) sample of $Ta_6Br_{14} \cdot 8H_2O$ was dissolved in 100 ml of methanol and 100 ml of distilled water and filtered. After filtering, 0.19 g (0.75 mmol) of iodine crystals were added to oxidize the Ta_6Br_{12} cation while it was in solution. This solution was added to a 3.92 g (23.0 mmol) sample of p-toluenesulfonic acid dissolved in 200 ml of distilled water. No reaction was seen when all the complex was added, so 15.14 g (80.0 mmol) of solid p-toluenesulfonic acid was then added to the solution. Since no evidence of precipitation was observed, an additional 7.78 g (45.0 mmol) of p-toluenesulfonic acid was added and again no reaction was observed. Heating the reactants for forty minutes also did not bring about precipitation and so the solution was allowed to stand overnight. On the next day, fine, light brown crystals were seen in the beaker. They were filtered, washed three times with 50 ml of anhydrous ether, and dried in vacuo over phosphorus pentoxide. Yield: 1.83 g = 66.4%.

Analysis: Found: Ta, 39.41%; Br, 34.66%; C, 9.39%; H, 1.51%; Br/Ta, 11.90/6.00.

Calculated for $Ta_6Br_{12}(C_7H_7SO_3)_3 \cdot 11H_2O$: Ta, 39.39%; Br, 34.70%; C, 9.15%; H, 1.57%.

Preparation of $Nb_6Br_{12}(C_7H_7SO_3)_4 \cdot 9H_2O$

A filtered solution of 1.81 g (1.00 mmol) of $Nb_6Br_{14} \cdot 8H_2O$ in 100 ml of distilled water was oxidized by adding 0.14 g (0.55 mmol) of iodine. This oxidized solution was added with stirring to a solution of 3.92 g (23.0 mmol) of p-toluenesulfonic acid in 200 ml of distilled water. Since no reaction was observed, 15.14 g (80.00 mmol) of solid p-toluenesulfonic acid was added. Again no product was formed, and an additional 76.1 g (400 mmol) of the solid acid was added. The solution was now heated with stirring until its volume decreased to 150 ml. Thereafter hydrolysis products were removed by filtration, and oxygen was bubbled into the solution for two hours. No precipitate was formed. Two weeks later it was discovered that a black crystalline solid had formed. More of it was obtained when anhydrous ether was added to the solution. The product was filtered, washed three times with 15 ml portions of anhydrous ether, and dried in vacuo over phosphorus pentoxide.

Yield: 0.86 g = 36.4%.

Analysis: Found: Nb, 23.36%; Br, 40.60%;

Br/Nb, 12.13/6.00; C, 14.13%; H, 1.96%.

Calculated for $Nb_6Br_{12}(C_7H_7SO_3)_4 \cdot 9H_2O$: Nb, 23.59%;

Br, 40.57%; C, 14.23%; H, 1.96%.

Preparation of a Hydrated Hydroxide of the $(Ta_6Br_{12})^{2+}$ Cation

The preparation of this compound had been described before by Chapin.[9] It was subsequently used as a starting material in the attempted synthesis of a hydrated sulfate of the $(Ta_6Br_{12})^{2+}$ cation. A 2.31 g (1.00 mmol) sample of $Ta_6Br_{12} \cdot 8H_2O$ was dissolved in 20 ml of methanol and 80 ml of distilled water. To the filtered solution was added dropwise and with stirring 32.8 ml of a 0.1 M sodium hydroxide solution. After the precipitate had formed it was filtered washed three times with 10 ml of distilled water and twice with 50 ml of anhydrous ether, and dried in vacuo over phosphorus pentoxide.

Yield: 1.19 g = 53.8%.

Attempt to Prepare a Hydrated Sulfate of the $(Ta_6Br_{12})^{n+}$ Ion Via $(Ta_6Br_{12})(OH)_2 \cdot nH_2O$

In preliminary experiments the formation of green, rectangular plates in the reaction between $Ta_6Br_{14} \cdot 8H_2O$ and ammonium sulfate had been observed. Therefore, this attempt was made to prepare a sulfate of the $(Ta_6Br_{12})^{2+}$ cation from $(Ta_6Br_{12})(OH)_2 \cdot nH_2O$ and sulfuric acid. A 0.36 g (0.20 mmol) sample of $(Ta_6Br_{12})(OH)_2 \cdot nH_2O$ was dissolved in 10 ml of methanol and 50 ml of distilled water. It was filtered and added dropwise to a 20 ml sample of dilute sulfuric acid. No reaction was noted as the $(Ta_6Br_{12})(OH)_2 \cdot nH_2O$ was added. Heat was then applied for thirty minutes and the presence of

shiny, brown crystals was observed as the solution cooled. The precipitate was filtered, washed twice with 50 ml of dilute sulfuric acid, and twice with 50 ml of anhydrous ether before it was dried _in vacuo_ over phosphorus pentoxide. Yield: 2.56 g.

No analysis was made since the brown color of the product indicated the presence of oxidized (Ta_6Br_{12}) cations.

Preparation of $(Ta_6Br_{12})(SO_4)_2 \cdot nH_2O$

This compound has been made before by McCarley, Hughes, Cotton, and Zimmerman.[15] The following procedure is an improved method of preparation.

A 2.34 g (1.00 mmol) sample of $Ta_6Br_{14} \cdot 8H_2O$ was dissolved in 100 ml of distilled water and filtered. Then a 0.24 g (1.00 mmol) sample of ammonium peroxydisulfate was dissolved in 20 ml of distilled water and added dropwise to the filtered cluster hydrate. Brown, shiny crystals were seen as soon as all the ammonium peroxydisulfate was added to the complex. This product was filtered, washed twice with 15 ml of distilled water and twice with anhydrous ether and dried _in vacuo_ over phosphorus pentoxide. Yield: 1.24 g = 55.5%.

Analysis: Found: Ta, 45.05%; Br, 38.98%; Br/Ta, 11.76/6.00. Calculated for $Ta_6Br_{12}(SO_4)_2 \cdot 11H_2O$: Ta, 44.59%; Br, 39.38%.

Preparation of $(Nb_6Br_{12})SO_4 \cdot 11H_2O$

A 1.83 g (1.10 mmol) sample of $Nb_6Br_{12} \cdot 8H_2O$ was dissolved in 100 ml of distilled water and filtered. A 0.59 g (4.0 mmol) sample of sodium sulfate was added to the filtered cluster hydrate and some new material was seen in the reaction beaker. Further additions of sodium sulfate resulted in precipitation of the new compound. A total of 0.58 g (4.0 mmol) of sodium sulfate was added in two batches to further precipitate a very light brown material. It was filtered, washed three times with 15 ml of acetone, and dried in vacuo over phosphorus pentoxide for fifteen minutes. Yield: 1.34 g = 74.7%.

Analysis: Found: Nb, 31.04%; Br, 52.63%; S, 1.99%; Br/Nb, 11.83/6.00; S/Nb, 1.11/6.00.

Calculated for $(Nb_6Br_{12})SO_4 \cdot 11H_2O$: Nb, 30.79%; Br, 52.96%; S, 1.77%.

Reaction of Sodium Formate with $Ta_6Br_{14} \cdot 8H_2O$

A filtered solution of 2.35 g (1.00 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ in 100 ml of distilled water and 100 ml of methanol was added dropwise and with stirring to a solution of 1.34 g (2.00 mmol) of sodium formate in 100 ml of distilled water. Since only a small quantity of product was formed, 5.36 g (80.0 mmol) and thereafter 26.8 g (400 mmol) of sodium formate was added as a solid. Shiny dark green crystals were observed after the reaction mixture had been

stirred overnight. The product was filtered, washed with distilled water, and dried _in vacuo_ over phosphorus pentoxide.

Yield: 1.87 g = 79.6%.

Analysis: Found: Ta, 48.28%; Br, 39.45%;

Br/Ta, 11.10/6.00; C, 1.59%; H, 0.92%.

Calculated for $[(Ta_6Br_{11}HCO_2)(HCO_2)_2(H_2O)_4] \cdot 4H_2O$:

Ta, 48.38%; Br, 39.17%; C, 1.61%; H, 0.85%.

Reaction of Sodium Formate and Formic Acid with $Nb_6Br_{14} \cdot 8H_2O$

A 1.83 g (1.00 mmol) sample of $Nb_6Br_{14} \cdot 8H_2O$ was dissolved in 50 ml of methanol and 50 ml of distilled water and filtered. The solution was acidified by adding 10 ml of formic acid, and then 10.01 g (147.0 mmol) of sodium formate was added. Precipitation occurred after one hour had elapsed. Dark green, shiny crystals were seen in the reaction beaker. They were filtered, washed with 20 ml of distilled water and three times with 15 ml of anhydrous ether, and dried _in vacuo_ over phosphorus pentoxide.

Yield: 1.10 g = 61.4%.

Analysis: Found: Nb, 31.89%; Br, 52.91%;

Br/Nb, 11.45/6.00; C, 2.82%; H, 1.07%.

Calculated for $Nb_6Br_{12}(HCO_2)_2 \cdot 2HCO_2H \cdot 6H_2O$: Nb, 30.86%;

Br, 53.08%; C, 2.66%; H, 1.00%.

In a previous attempt in which mainly sodium formate was used only white hydrolysis or decomposition products were formed.

Reaction of Ammonium Acetate with $Ta_6Br_{14} \cdot 8H_2O$

Preliminary experiments had shown that an acetate derivative of an oxidized Ta_6Br_{12} cation appeared to be insoluble in distilled water. Therefore a filtered solution of 2.29 g (1.00 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ in 50 ml of distilled water and 50 ml of methanol was oxidized by adding to it 0.62 g (2.44 mmol) of iodine. The oxidized solution was added to 1.58 g (20.0 mmol) of ammonium acetate in 100 ml of distilled water, and precipitation occurred immediately. However, the fine crystalline product was dark green in color, indicating the presence of non-oxidized cluster material. After allowing the reaction mixture to stand overnight, the product was filtered, washed three times with 50 ml of anhydrous ether, and dried in vacuo over phosphorus pentoxide.

Yield: 0.81 g.

Analysis: Found: Ta, 44.18%; Br, 33.04%; Br/Ta, 9.13/6.00. The analysis showed that the desired product was not formed.

Reaction of Sodium Nitrite with $Ta_6Br_{14} \cdot 8H_2O$

To a solution of 2.38 g (1.00 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ dissolved in 50 ml of distilled water was slowly added 0.75 g (11.0 mmol) of solid sodium nitrite. A new compound was formed after five minutes of stirring. The dark green material was filtered, washed with 15 ml of anhydrous ether, and dried in vacuo over phosphorus pentoxide.

Yield: 1.71 g = 79.0%.

Analysis: Found: Ta, 46.00%; Br, 39.40%; Br/Ta, 11.61/6.00.
Calculated for $Ta_6Br_{12}(NO_2)_2 \cdot 14H_2O$: Ta, 45.45%; Br, 40.14%.

In a second attempt, a filtered solution of 2.40 g
(1.00 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ in 100 ml of distilled water was
added to a 0.73 g (10.0 mmol) sample of sodium nitrite dis-
solved in 200 ml of distilled water. A precipitate was
formed which appeared to be very fine in texture and dark
brown in color. The crystals were filtered, washed three
times with 50 ml of distilled water, and dried in vacuo
over phosphorus pentoxide.

Yield: 0.67 g.

No analysis of this product was made.

Reaction of Sodium Nitrite with $Nb_6Br_{14} \cdot 8H_2O$

A 1.81 g (1.00 mmol) sample of $Nb_6Br_{14} \cdot 8H_2O$ was
dissolved in 100 ml of methanol and 100 ml of distilled
water. This solution was filtered and added dropwise to
0.76 g (11.0 mmol) of sodium nitrite dissolved in 100 ml
of distilled water. A precipitate was formed immediately.
The very fine olive-green material was filtered, washed
three times with 50 ml of distilled water, and dried in vacuo
over phosphorus pentoxide.

Yield: 0.07 g.

This quantity was not sufficient to run an analysis.

Reaction of $Ta_6Br_{14} \cdot 8H_2O$ with Potassium Cyanate

Preliminary experiments had shown that two cyanate derivatives of the Ta_6Br_{12} cation were formed, a green water soluble material and a brown oxidized water insoluble material. In an attempt to obtain the latter product, a filtered solution of 2.34 g (1.00 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ in 50 ml of methanol and 50 ml of distilled water was oxidized by adding to it a solution of 0.04 g (0.5 mmol) of potassium bromate in 25 ml of distilled water. The oxidized solution was added dropwise to a solution of 1.65 g (20.0 mmol) of potassium cyanate in 125 ml of distilled water. Since only a small amount of a green product was formed, 6.51 g (80.0 mmol) of solid potassium cyanate was added. No further precipitation was observed, and therefore the solution was heated for thirty minutes. A large amount of an orange-brown precipitate was formed. After the mixture was stirred overnight, it was seen that the precipitate was whitish in color. It was filtered, washed three times with 50 ml of acetone, and dried in vacuo over phosphorus pentoxide. The dried product was white indicating decomposition of the Ta_6Br_{12} cation.

Yield: 1.43 g.

Reaction of Ammonium Thiocyanate with $Ta_6Br_{14} \cdot 8H_2O$

A filtered solution of 2.31 g (1.00 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ in 50 ml of methanol and 50 ml of distilled water was added dropwise and with stirring to a solution of 1.56 g (20.0 mmol) of ammonium thiocyanate in 100 ml of distilled water. No precipitate was observed, so 6.12 g (80.0 mmol) of potassium thiocyanate was added and the solution was stirred overnight. Since preliminary experiments had resulted in orange colored thiocyanate derivaties of oxidized Ta_6Br_{12} cations, 0.133 g (0.52 mmol) of iodine, I_2, was added to the solution, resulting in the formation of a light brown precipitate. This material was filtered but it was lost when anhydrous ether was used to wash the solid.

A second attempt of this synthesis was also futile even though iodine was used to oxidize the $(Ta_6Br_{12})^{2+}$ cation. A light brown precipitate was formed but repeated attempts to filter it over sintered glass failed. The reaction mixture was left to evaporate but this resulted in decomposition of the product upon standing for several days.

Reaction of the Disodium Salt Monohydrate of Iminodiacetic Acid with $Ta_6Br_{14} \cdot 8H_2O$

A solution of 2.33 g (1.00 mmol) of $Ta_6Br_{14} \cdot 8H_2O$ in 100 ml of methanol and 100 ml of distilled water was filtered into a solution of 3.92 g (20.0 mmol) of the disodium salt monohydrate of iminodiacetic acid in 100 ml of distilled water. A green product was recovered from a brown solution.

The product was filtered and washed three times with 50 ml of acetone. After drying it was seen that the main part of the product was white and therefore, did not contain the $(Ta_6Br_{12})^{2+}$ cation.

A second attempt was more successful than the previous one. Less solution was used to dissolve the reactants. A 2.34 g (1.00 mmol) sample of $Ta_6Br_{14} \cdot 8H_2O$ was dissolved in 40 ml of distilled water and filtered. To the filtrate 1.97 g (10.0 mmol) of the disodium salt monohydrate of iminodiacetic acid dissolved in 50 ml of distilled water was added in small portions. The light green product was filtered, washed three times with 20 ml of acetone, and dried in vacuo over phosphorus pentoxide.

Yield: 1.13 g.

Analysis: Found: Ta, 47.77%; Br, 36.05%;

Br/Ta, 10.25/6.00.

The analysis showed that the desired product was not formed.

CHAPTER IV

RESULTS AND DISCUSSION

Reactions of Hydrated Halides $M_6X_{14} \cdot 8H_2O$ With Neutral Ligands

Acetonitrile Compounds

Two new compounds $[(Ta_6Cl_{12})Cl_2(CH_3CN)_4]$ and $[(Ta_6Br_{12})Br_2(CH_3CN)_4]$ were synthesized and characterized as stable, and well defined complexes. They were found to precipitate when solutions of hydrated halides $Ta_6X_{14} \cdot 8H_2O$ in equal volumes of methanol and acetonitrile were evaporated by heating to about one fourth of their original volume.

Four acetonitrile complexes $[(M_6X_{12})X_2(CH_3CN)_4]$ have been synthesized from the starting material $[(M_6X_{12})X_2(H_2O)_4] \cdot 4H_2O$. In general, it is difficult to replace coordinated water molecules from this starting material. However, the replacement readily occurs when the replacing ligand is acetonitrile. This may be due to a hydrolysis reaction of acetonitrile which removes water from the equilibrium mixture, thus leaving only acetonitrile molecules in the presence of the (M_6X_{12}) central cation.

Complexes of 1,2,6-Trimethyl-4-Pyridone

Three new complexes $[(Nb_6Cl_{12})Cl_2L_4]$,

$[(Ta_6Cl_{12})Cl_2L_4]$ and $[(Mo_6Cl_8)Cl_4L_2]$ with 1,2,6-trimethyl-4-pyridone as the ligand L were obtained as microcrystalline precipitates when ethanolic solutions of the ligand were added to methanolic solutions of $Nb_6Cl_{14}\cdot 8H_2O$, $Ta_6Cl_{14}\cdot 8H_2O$, and Mo_6Cl_{12}.

The same method did not lead to the formation of the corresponding bromide complexes of niobium and tantalum, and the solid products that were eventually obtained did not correspond to the expected formula $[(M_6Br_{12})Br_2L_4]$.

The compound 1,2,6-trimethyl-4-pyridone was chosen as a ligand because it has the same geometry in the vicinity of its oxygen donor atom as pyridine-N-oxide.
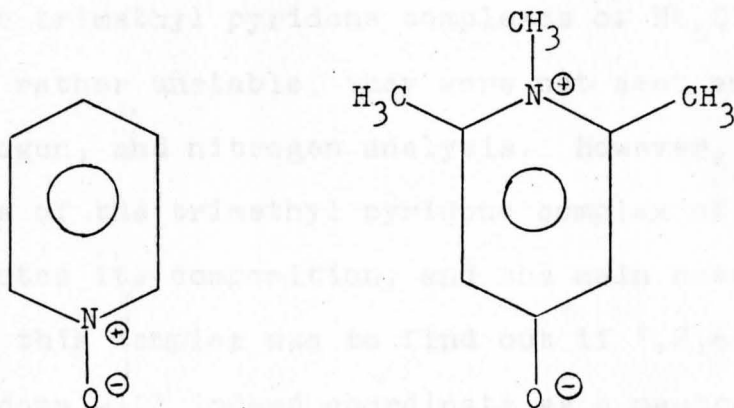
pyridine-N-oxide   1,2,6-trimethyl-4-pyridone

Fig. 2. The structures of pyridine-N-oxide and 1,2,6-trimethyl-4-pyridone.

However, its complexes are not as easily formed as those of pyridine-N-oxide, and they appear to be less stable. One batch of the trimethyl pyridone complex of Ta_6Cl_{14} decomposed violently when exposed to the open air after drying over phosphorus pentoxide. The dark green product crystals ignited, became red hot, and emitted white billowing smoke. A second smaller batch did not decompose when exposed to the air after drying. However, when kept in a vial for storage, it changed color from avocado green to light reddish brown within two weeks.

The compound $[(Mo_6Cl_8)Cl_4(C_8H_{11}ON)_2]$ is the only complex based on an M_6X_8 central cation that was synthesized in this work. It appears to be stable over extended periods of time and no indications of decomposition could be observed even after several months.

Since the trimethyl pyridone complexes of Nb_6Cl_{14} and Ta_6Cl_{14} were rather unstable, they were not sent away for carbon, hydrogen, and nitrogen analysis. However, the complete analysis of the trimethyl pyridone complex of Mo_6Cl_{12} corroborates its composition, and the main reason for synthesizing this complex was to find out if 1,2,6-trimethyl-4-pyridone will indeed coordinate as a neutral ligand to hexanuclear central cations.

Other Reactions With Neutral Ligands

Other reactions with neutral ligands L did not lead to the expected complexes $[(M_6X_{12})X_2L_4]$.

With 2,6-dimethyl-4-pyrone, which resembles
pyridine-N-oxide in the vicinity of its oxygen donor atom,
a product with an 11/6 Cl/Nb ratio was obtained.
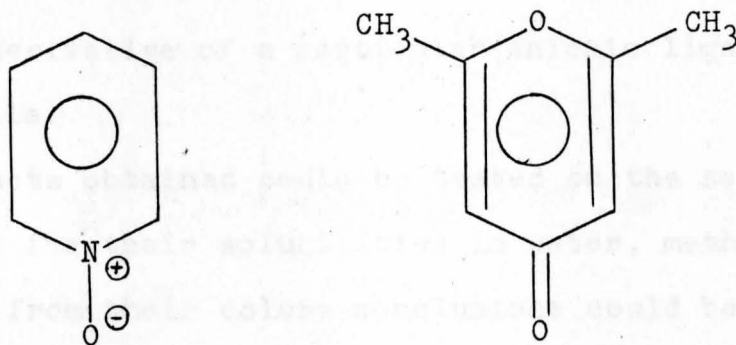
pyridine-N-oxide   2,6-dimethyl-4-pyrone

Fig. 3.   The structures of pyridine-N-oxide
and 2,6-dimethyl-4-pyrone.

Attempts to use benzophenone and urea as ligands
yielded only unreacted starting materials, and in a reaction
with p-aminophenol, too little product was obtained to run
an analysis. All in all it appears that only a few neutral
ligands can replace water in $[(M_6X_{12})X_2(H_2O)_4]\cdot 4H_2O$. These
include dimethylsulfoxide,[25] dimethylformamide,[25] triphenyl-
arsine oxide,[25] triphenylphosphine oxide,[25] pyridine-N-
oxide,[25,26] pyridine,[3] acetonitrile,[3,26]
1,2,6-trimethyl-4-pyridone,   and propionitrile (C_2H_5CN).[3]

Preliminary Experiments Involving
Anionic Ligands

The preliminary experiments that were performed on a microscopic scale made it possible to rapidly determine whether or not there was a chance to prepare a crystalline complex cluster derivative of a particular anionic ligand on a macroscopic scale.

The products obtained could be tested on the same microscopic scale for their solubilities in water, methanol, and ethanol, and from their colors conclusions could be drawn with respect to the oxidation states of their M_6X_{12} central cations. The information thus gained was extremely valuable for the design of subsequent full-scale preparations.

Not all microscopic scale experiments resulted in successful full-scale preparations. Solutions used on a small scale were more concentrated and the solvent employed evaporated rather fast. That resulted in the rapid formation of solid products without giving the M_6X_{12} cations sufficient time to decompose. Also, the formation of complexes of oxidized M_6X_{12} cations seemed to be more favored in the preliminary experiments, probably because small samples are more easily oxidized by air.

Reactions of Hydrates $M_6X_{14} \cdot 8H_2O$ With Anionic Ligands

The reactions of hydrates $M_6X_{14} \cdot 8H_2O$ with anionic ligands led to a number of new, well crystallized complexes.

Oxalate Compounds

Oxalate compounds of the formula $(M_6X_{12})C_2O_4 \cdot 11H_2O$ could be obtained only with the Ta_6Br_{12} and Nb_6Br_{12} central cations. Corresponding reactions involving Nb_6Cl_{12} and Ta_6Cl_{12} central cations did not lead to solid products.

A mull spectrum of $Ta_6Br_{12}C_2O_4 \cdot 11H_2O$ (Table 2) showed maxima at 12.9, 14.8, and 27kK. Analytical data, the emerald green color of the complex, and a comparison of the spectral data with Spreckelmeyer's compilation[31] characterize the complex as a derivative of the dipositive Ta_6Br_{12} central cation.

For $(Nb_6Br_{12})C_2O_4 \cdot 11H_2O$, the spectrum (Table 3) showed maxima at 15.5, 22.4, 32.6, and 42.5kK. These spectral data do not give a clear indication of the oxidation state of the Nb_6Br_{12} central cation, particularly since Spreckelmeyer's data on $(Nb_6Br_{12})^{n+}$ derivatives[30] are not quite complete. However, since the analytical data indicate a composition analogous to $(Ta_6Br_{12})C_2O_4 \cdot 11H_2O$, it appears to be justified to formulate the complex as an $(Nb_6Br_{12})^{2+}$ derivative.

TABLE 2

SOLID STATE SPECTRA OF COMPOUNDS CONTAINING $(Ta_6Br_{12})^{n+}$ CATIONS

Compound	Wave Numbers in Kilokaisers							
$Ta_6Br_{14} \cdot 8H_2O$ [a]			12.8	14.9	20.7	23.7	27.9	35.4
$Ta_6Br_{12}C_2O_4 \cdot 11H_2O$ [b]			12.1	14.8			27.0	
$(Ta_6Br_{11}HCOO)(HCOO)_2 \cdot 8H_2O$ [b]			12.1	14.9			27.1	
$Ta_6Br_{15} \cdot 7H_2O$ [a]	10.8	11.5	13.5		19.2	23.8	27.0 33.9	
$Ta_6Br_{12}(C_7H_7SO_3)_3 \cdot 11H_2O$ [b]			13.4				26.6	
$Ta_6Br_{12}(SO_4)_2 \cdot nH_2O$ [b]			13.6				26.6	
$Ta_6Br_{16} \cdot 7H_2O$ [a]	10.7	11.7			19.7	23.4 26.7		

[a] B. Spreckelmeyer, Z. Anorg. Allg. Chem., 365, 225 (1969).

[b] Values determined in this work.

TABLE 3

SOLID STATE SPECTRA OF COMPOUNDS CONTAINING $(Nb_6Br_{12})^{n+}$ CATIONS

Compound	Wave Numbers in Kilokaisers							
$Nb_6Br_{14} \cdot 8H_2O$ [a]			10.1	16.5	20.8	22.8		34.3	
$Nb_6Br_{12}C_2O_4 \cdot 11H_2O$ [b]			10.2			22.9	33.7		41.7 43.8
$Nb_6Br_{12}SO_4 \cdot 11H_2O$ [b]			10.2			22.9	33.9		41.5
$Nb_6Br_{12}(HCOO)_2 \cdot (HCOOH)_2 \cdot 6H_2O$ [b]			10.2			22.6	33.0		41.2 43.3
$Nb_6Br_{12}(C_7H_7SO_3)_4 \cdot 9H_2O$ [b]			10.3		22.2 32.5				41.3
$(pyH)_2(Nb_6Br_{12})Cl_6$ [a]	8.4	9.7			20.6		33.9		

[a]B. Spreckelmeyer, Z. Anorg. Allg. Chem., 365, 225 (1969).

[b]Values determined in this work.

Carbonate Compounds

The carbonate derivatives of $M_6Br_{14} \cdot 8H_2O$ precipitated very easily but different compounds were obtained from $Ta_6Br_{14} \cdot 8H_2O$ and $Nb_6Br_{14} \cdot 8H_2O$. The tantalum derivative was formulated as $Ta_6Br_{12}CO_3 \cdot 8H_2O$ while the niobium derivative was found to be $Nb_6Br_{12}CO_3 \cdot 4H_2O$. The $Ta_6Br_{12}CO_3 \cdot 8H_2O$ compound appears to be stable whereas $Nb_6Br_{12}CO_3 \cdot 4H_2O$ decomposed giving off HBr after being stored in a vial for several days.

One reason for the decomposition of $(Nb_6Br_{12})CO_3 \cdot 4H_2O$ could be the reaction of water molecules with bromide ions from the $Nb_6Br_{12}^{2+}$ central cation. In such a reaction, the bromide ions in the Nb_6Br_{12} group would be replaced by hydroxide ions, and the hydrogen bromide set free might react with carbonate terminal ligands, replacing them with bromide ions. This is corroborated by the fact that after it was allowed to stand for six weeks, the product had lost all carbonate.

In addition, hard drying might contribute to the decomposition of the compound. A batch of $(Nb_6Br_{12})CO_3 \cdot 4H_2O$ that had been dried for two hours in a dynamic vacuum was found to have a Br/Nb ratio of only 11.07/6.

No spectral data were taken for the carbonate complexes. However, the green color of solid $(Ta_6Br_{12})CO_3 \cdot 8H_2O$ should be taken as support for the presence of the dipositive (Ta_6Br_{12}) central cation.

The carbonate complexes of M_6X_{12} central cations might have some preparative importance. Since they are so easily precipitated they might be useful for the isolation and purification of cluster material when this material is part of a reaction mixture.

p-Toluenesulfonic Acid Complexes

Analytical data for the p-toluenesulfonate of Ta_6Br_{12} indicated the composition $(Ta_6Br_{12})(C_7H_7SO_3)_3 \cdot 11H_2O$. This would point to a tripositive charge for the Ta_6Br_{12} central cation, which is is also indicated by the fact that the material is brown and not emerald green. The spectrum showed (Table 2) maxima at 13.4, 26.6, and 43.8kK, and a comparison with Spreckelmeyer's data for $Ta_6Br_{15} \cdot 7H_2O$ confirms the tripositive charge for the central cation.

The conditions under which the toluenesulfonate of Ta_6Br_{12} was prepared did not lead to the formation of a corresponding complex of Nb_6Br_{12}. Only when a large excess of solid toluenesulfonic acid was added and ether was employed as a precipitating agent was a solid product obtained. It was different both in its formula and oxidation state from the Ta_6Br_{12} complex. Analytical data would support two different formulas for this product:

$(Nb_6Br_{12})(C_7H_7SO_3)_4 \cdot 9H_2O$ with a fourfold positive cation
and $(Nb_6Br_{12})(C_7H_7SO_3)_2 \cdot 2C_7H_7SO_3H \cdot 9H_2O$ with a dipositive
Nb_6Br_{12} unit. Spectral measurements indicated maxima at
10.3, 22.2, 32.5, and 41.3kK (Table 3). From these
data it was impossible to draw definite conclusions about
the oxidation state of the central cation. The formula
$(Nb_6Br_{12})(C_7H_7SO_3)_4 \cdot 9H_2O$ has been used since the analytical
data appeared to favor it slightly.

Sulfate Complexes

Preliminary experiments had resulted in a green
tantalum bromide sulfate, the green color indicating the
presence of dipositive Ta_6Br_{12} cations. However, in full-
scale preparations only a brown oxidized product could be
obtained, even though no oxidizing agent was employed.
Apparently the green sulfate is more soluble in water than
the microscopic experiments had indicated. If a reaction
mixture is allowed to stand, air oxidation of the Ta_6Br_{12}
cation rapidly leads to the formation of the insoluble brown,
oxidized sulfate complex.

This brown compound appears to be identical with a
product made by McCarley, Hughes, Cotton, and Zimmerman[15]
who described it as a sulfate derivative of a fourfold
positive Ta_6Br_{12} cation. The procedure cited in the experi-
mental section of this work is an improved method of prepa-
ration. Ammonium peroxydisulfate oxidizes the cluster

cation and, at the same time, supplies the sulfate ligand. Tantalum and bromide analyses agree with McCarley's values.

The spectrum of this brown tantalum bromide shows maxima at 13.6 and 25.6kK which points towards a tripositive Ta_6Br_{12} cation. A closer evaluation of McCarley's analytical data[15] shows a Br/Ta ratio of 11.67/6.00 and an SO_4/Ta ratio of 1.75/6.00, which amounts to a total of 15.18 negative charges per six tantalum atoms. It appears that some sulfate anions have replaced bridging ions of the Ta_6Br_{12} central cation, and that the central cation indeed corresponds to a tripositive Ta_6X_{12} moity, even though the analytical data place it close to $Ta_6Br_{12}(SO_4)_2 \cdot nH_2O$.

The spectrum of $(Nb_6Br_{12})SO_4 \cdot 11H_2O$ shows maxima at 10.2, 22.9, 33.9, and 41.5kK. It agrees very well with the spectrum found for $Nb_6Br_{12}C_2O_4 \cdot 11H_2O$. This agreement alone would not be sufficient for a conclusive identification of the oxidation state of the Nb_6Br_{12} central cation. However, analytical data clearly point to the formula $Nb_6Br_{12}SO_4 \cdot 11H_2O$ and therefore to a dipositive charge for for the Nb_6Br_{12} cation.

Reaction of Sodium Formate with $Ta_6Br_{14} \cdot 8H_2O$

The product obtained in this reaction was found to have a bromine to tantalum ratio of 11.10/6 and a carbon to tantalum ratio of 2.97/6. The spectrum showed maxima at 13.1, 14.9, and 27.1kK indicating a dipositive charge for the (Ta_6Br_{12}) central cation. This can only be explained

by assuming that one bridging bromide ion of the Ta_6Br_{12} central cation has been replaced by a formate ion, resulting in a $(Ta_6Br_{11}HCOO)^{2+}$ central cation. Therefore the compound should be formulated as $(Ta_6Br_{11}HCO_2)(HCO_2)_2 \cdot 8H_2O$.

Reaction of Sodium Formate and Formic Acid With $Nb_6Br_{14} \cdot 8H_2O$

A spectrum for this product showed maxima at 10.2, 22.6, 33.0, 41.2, and 43.3kK. From this no definite conclusions could be drawn with regard to the oxidation state of the central cation. The analytical data obtained would allow a formulation both as $Nb_6Br_{12}(HCOO)_2 \cdot 2HCOOH \cdot 6H_2O$ with a two-fold positive charge for the (Nb_6Br_{12}) central cation and as $Nb_6Br_{12}(HCOO)_4 \cdot 6H_2O$ with a fourfold positive charge for the cluster cation. The green color of the product supports the former formulation.

Reaction of Ammonium Acetate with $Ta_6Br_{14} \cdot 8H_2O$

The product obtained in this reaction was found to have a bromine to tantalum ratio of 9.13/6. This may indicate that bromide ions have been removed from the Ta_6Br_{12} unit and replaced by acetate ions. Such a replacement may then lead to the breakdown of the M_6 cluster. In a second product obtained by a similar method disintegration of the M_6X_{12} cation apparently had proceeded even further as indicated by a 3.34/6 Br/Ta ratio and the extremely light color of the product.

Reaction of Ammonium Thiocyanate with $Ta_6Br_{14} \cdot 8H_2O$

Preliminary experiments resulted in an orange-brown product indicating an oxidation state for the (Ta_6Br_{12}) central cation greater than 2+. On a large scale a brown precipitate was formed but it was lost when anhydrous ether was used to wash the crystalline material. In the second trial, the brown precipitate was again formed indicating that 2+ material was not formed. The material was so fine in texture that repeated attempts to filter it over sintered glass failed. The solution was left to evaporate since filtering attempts failed. Before the solution evaporated, the solid material began to decompose as indicated by a lightening of its color.

Reaction of Disodium Salt Monohydrate of Iminodiacetic Acid with $Ta_6Br_{14} \cdot 8H_2O$

The product obtained was found to have a bromine to tantalum ratio of 10.25/6.00 indicating partial decomposition of the (Ta_6Br_{12}) central cation, and it was visibly different from the large dark green crystals obtained during the microscopic experiments. The decomposition could be caused by the fact that the solution of the anion is basic due to hydrolysis.

CHAPTER V

CONCLUSIONS

In this work, attempts were made to synthesize coordination compounds with $(M_6X_{12})^{n+}$ central cations from hydrates of the formula $[(M_6X_{12})X_2(H_2O)_4]\cdot 4H_2O$ by either replacing water terminal ligands by other neutral ligands or replacing halide terminal ligands by other anionic ligands.

The experiments showed that water molecules attached to M_6X_{12} central cations are extremely difficult to replace by other neutral ligands. Only a few complexes of the formula $[(M_6X_{12})X_2L_4]$ could be prepared. They did not precipitate out sufficiently well to be used for the purpose of isolating, separating, or purifying M_6X_{12} cluster material, and they were not sufficiently well crystallized to be used for X-ray structure investigations.

Well crystallized complexes were obtained, however, when the terminal halide ligands of hydrates $[(M_6X_{12})X_2(H_2O)_4]\cdot 4H_2O$ were replaced by other anionic ligands. Some of the complexes thus obtained appeared to be sufficiently well crystallized to be used for single crystal structure determinations. A number of them appear to be suitable for isolating (M_6X_{12}) cluster material from an aqueous reaction mixture, particularly the carbonate derivatives of

$(Nb_6Br_{12})^{2+}$ and $(Ta_6Br_{12})^{2+}$, which are very well crystallized and very insoluble in water.

The carbonate derivatives could gain some preparative importance since they can probably be used for the preparation of pure hydrated compounds $(M_6X_{12})Y_2 \cdot aq$ by reaction with acid HY:

$$(M_6X_{12})CO_3 \cdot aq + 2HY \longrightarrow (M_6X_{12})Y_2 \cdot aq + H_2O + CO_2 \qquad (2)$$
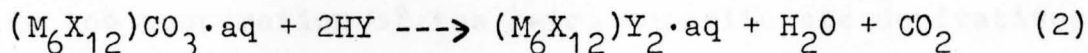
A method of this kind is generally used for the preparation of pure transition element compounds. Additional work is needed in the area of the carbonate derivatives, particularly since no attempt was made to prepare the hydrated carbonates of the $(Nb_6Cl_{12})^{2+}$ and $(Ta_6Cl_{12})^{2+}$ cations.

This work has also shown that certain anionic ligands are selective in their reactions with M_6X_{12} cluster cations. Therefore they appear to be useful for separating M_6X_{12} cluster cations of different kinds. When the oxalate ion was used as a ligand it was found that the bromide cluster derivatives of the formula $(M_6Br_{12})(C_2O_4) \cdot nH_2O$ would crystallize out. However, when solutions of chlorides $(M_6Cl_{12})Cl_2 \cdot nH_2O$ were reacted with ammonium oxalate, no solid reaction product was obtained. Therefore the oxalate ion should be able to separate the $(M_6Br_{12})^{2+}$ cation from the $(M_6Cl_{12})^{2+}$ cation if both are present.

Also the p-toluenesulfonic acid was found to be selective in its reactions with cluster cations. Experiments showed that from aqueous solution a well crystallized derivative $(Ta_6Br_{12})(C_7H_7SO_3)_3 \cdot 11H_2O$ of the $(Ta_6Br_{12})^{3+}$

cation was obtained. When the same procedure was used, no p-toluenesulfonate of an $(Nb_6Br_{12})^{n+}$ cation could be obtained. A p-toluenesulfonate of an $(Nb_6Br_{12})^{n+}$ cation was obtained only under very different conditions, and it had a stoichiometry different from that of its $(Ta_6Br_{12})^{n+}$ counterpart. Considering the different reaction conditions involved in the preparation of the p-toluenesulfonate derivatives, it appears to be safe to say that this ligand could be used to separate the $(Ta_6Br_{12})^{n+}$ cluster cation from the $(Nb_6Br_{12})^{n+}$ cation.

Analytical results for some of the products prepared in this work showed halogen to metal ratios that were smaller than the expected 12/6. This indicates the removal of bridging halogens from M_6X_{12} central cations. In basic solutions bridging halogens are probably replaced by hydroxide ions and this replacement is the first step in the decomposition of M_6X_{12} cluster cations that is generally observed in basic solution.[34] Since some of the anionic ligands were used in the form of their alkali salts and since the solutions of these salts are basic due to hydrolysis, low halogen to metal ratios for some of the products obtained in this work might simply be due to displacement of bridging halogens by hydroxide ions.

However, this does not apply to the product of the reaction between $Ta_6Br_{14} \cdot 8H_2O$ and sodium formate. The formula $(Ta_6Br_{11}HCOO)(HCOO)_2 \cdot 8H_2O$ derived from analytical and spectral data suggests that on the average, one bridging

halogen of the M_6X_{12} central cation has been replaced by a formate ion.

Substantial exchange of bridging halogens by acetate ions may occur in the reaction between $Ta_6Br_{14} \cdot 8H_2O$ and ammonium acetate as suggested by the low halogen to metal ratio, 9.3/6, of the product. Since this reaction occurs in a neutral solution, replacement of bridging halogens by hydroxide ions appears highly unlikely.

The replacement of bridging halogens may be assumed to proceed stepwise, and it is likely that some of the products isolated are actually mixtures with different degrees of substitution. Substitution of bridging halogens will ultimately lead to a breakdown of the cluster cation as suggested by the very light color of some of the reaction products.

The microscopic method that was developed to check in a short time if solid M_6X_{12} derivatives may be formed by a particular anion proved to be extremely valuable. It promises to be of great assistance in future preparations of coordination compounds based on $(M_6X_{12})^{n+}$ central cations.

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