

ABSTRACT

SYNTHESIS OF SOME POLYNUCLEAR NIOBIUM HALIDES

by

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A variety of methods were investigated for the preparation of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$. This hydrate is the starting material for the synthesis of coordination compounds based on hexanuclear $(\text{Nb}_6\text{Cl}_{12})^{n+}$ central cations. Previous methods for its preparation were cumbersome, required expensive equipment, or supplied the hydrate only in small quantities.

An efficient and convenient method for the synthesis of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ was developed. Conproportionation of niobium pentachloride with excess niobium metal and with sodium chloride in sealed Vycor tubes supplies the ternary halide $\text{Na}_4\text{Nb}_6\text{Cl}_{18}$. Upon extraction with water, $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ is obtained in yields up to 92%.

The new coordination compounds $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_4] \cdot 1.5(\text{C}_5\text{H}_5\text{N})$, $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{C}_2\text{H}_5\text{CN})_4]$, and $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]$ were synthesized and characterized.

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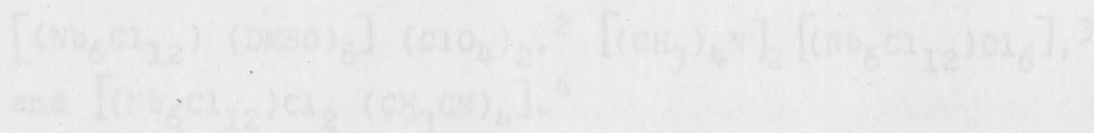
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cations. $(\text{M}_6\text{X}_{12})^{n+}$ cluster cations consist of metal-metal bonded M_6 octahedra with twelve halogens bridging over the octahedral edges.¹ Each metal atom has one site available for attachment of a terminal ligand, and positive, negative, and neutral complexes with the central cation in different oxidation states may be prepared. Examples are:



It can be expected that complexes based on $(\text{M}_6\text{X}_{12})^{n+}$ central cations exhibit some interesting features.

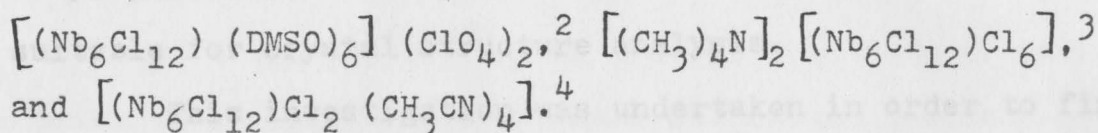
$(\text{M}_6\text{X}_{12})^{n+}$ central cations equipped with a mixed set of terminal ligands, for example, are likely to be considerably distorted by the greater attraction between the stronger bonding terminal ligands and the particular metal atoms they are coordinated to. Such distortions, which can be investigated by X-ray structure analysis, may give some indication about the strength of the MO bonding system⁵ in the electron-deficient $(\text{M}_6\text{X}_{12})^{n+}$ cluster unit and about the ligand strength of various donors with respect to $(\text{M}_6\text{X}_{12})^{n+}$ central cations.

So far, only a few crystal structure determinations

CHAPTER I

INTRODUCTION

One of the most peculiar classes of coordination compounds is based on hexanuclear metal cluster cations $(M_6X_{12})^{n+}$ ($M=Nb, Ta$; $X=Cl, Br, I$; $n=2,3,4$) as central cations. $(M_6X_{12})^{n+}$ cluster cations consist of metal-metal bonded M_6 octahedra with twelve halogens bridging over the octahedral edges.¹ Each metal atom has one site available for attachment of a terminal ligand, and positive, negative, and neutral complexes with the central cation in different oxidation states may be prepared. Examples are:



It can be expected that complexes based on $(M_6X_{12})^{n+}$ central cations exhibit some interesting features.

$(M_6X_{12})^{n+}$ central cations equipped with a mixed set of terminal ligands, for example, are likely to be considerably distorted by the greater attraction between the stronger bonding terminal ligands and the particular metal atoms they are coordinated to. Such distortions, which can be investigated by X-ray structure analysis, may give some indication about the strength of the MO bonding system⁵ in the electron-deficient $(M_6X_{12})^{n+}$ cluster unit and about the ligand strength of various donors with respect to $(M_6X_{12})^{n+}$ central cations.

So far, only a few crystal structure determinations

have been made of coordination compounds based on $(M_6X_{12})^{n+}$ cluster cations. This is probably due to preparative difficulties.

Syntheses of $(M_6X_{12})^{n+}$ containing cluster compounds are based on the hydrates $M_6X_{14} \cdot 8H_2O$ or $[(M_6X_{12})X_2(H_2O)_4] \cdot 4H_2O$ as starting materials. Although these hydrates have been known for almost sixty years,^{6,7} previous methods used for their preparation have been inefficient, complicated and only supplied the hydrates in small quantities. Moreover, $(M_6X_{12})^{n+}$ cations tend to decompose in solution, and contamination by decomposition products makes it difficult to prepare sufficiently pure and well-crystallized products suitable for crystal structure analysis.

This investigation was undertaken in order to find an efficient method for the preparation of $Nb_6Cl_{14} \cdot 8H_2O$ and to attempt the preparation of some coordination compounds based on $(Nb_6Cl_{12})^{n+}$ cluster cations.

It is highly probable that the formula should have been $(Ta_6Cl_{12})Cl_2 \cdot 7H_2O$ and not $TaCl_2 \cdot 2H_2O$ as Chabrie wrote it.

Following the work of Chabrie and Chapin, Karned⁸ carried out an investigation to determine whether the compounds prepared by Chabrie and Chapin were only peculiar to tantalum or whether it was possible to obtain a similar niobium chloride. Using Chabrie's method, he obtained a compound which upon analysis was formulated as $(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$, exactly analogous to the bromide of the tantalum compound prepared by Chapin. In 1960, after a

CHAPTER II

REVIEW OF PREVIOUS WORK

Synthesis of Hydrates of the General Formula $M_6X_{14} \cdot 8H_2O$

Attempts to prepare lower-valent tantalum chlorides were initiated in 1907 by Chabrié,⁸ who reduced tantalum pentachloride by heating with sodium amalgam under an aspirator vacuum. From the reduction product, a green solution was extracted with dilute acid and evaporated to give a green crystalline powder. The compound was formulated as $TaCl_2 \cdot 2H_2O$ as determined from a single analysis of the material.

In 1910, Chapin,⁶ using Chabrié's method, prepared a tantalum bromide. However, analysis showed the compound to have a composition of $Ta_6Br_{14} \cdot 7H_2O$. Since the properties of Chabrié's chloride correspond very closely with that of the bromotantalum compound, it seems highly probable that the formula should have been $(Ta_6Cl_{12})Cl_2 \cdot 7H_2O$ and not $TaCl_2 \cdot 2H_2O$ as Chabrié wrote it.

Following the work of Chabrié and Chapin, Harned⁷ carried out an investigation to determine whether the compounds prepared by Chabrié and Chapin were only peculiar to tantalum or whether it was possible to obtain a similar niobium chloride. Using Chabrié's method, he obtained a compound which upon analysis was formulated as $(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$, exactly analogous to the bromide of the tantalum compound prepared by Chapin. In 1960, after a

period of almost fifty years, Harned et al⁹ prepared the compound again, this time by reducing the niobium pentachloride with cadmium metal and heating to a "red heat" under an aspirator vacuum. By the same method, they were also able to obtain minute quantities of the corresponding bromoniobium compound. So far the cadmium reduction has been the method most commonly used for the preparation of the hydrates.

Schäfer and Bauer¹⁰ in 1965, established the formula for tantalum chloride as being $Ta_6Cl_{14} \cdot 8H_2O$, instead of $Ta_6Cl_{14} \cdot 7H_2O$, by determination of tantalum, chlorine, water, and the oxidation number.

In 1968, Fleming¹¹ developed a variation of Harned's method that uses lithium chloride/potassium chloride melts for the reduction of niobium pentachloride with cadmium. This molten salt variation gives higher yields. Its disadvantage is that, upon extraction with water, vast amounts of foreign substances are introduced into the aqueous solution.

Another method developed by McCarley and coworkers¹² is based on the high-temperature disproportionation of Nb_3X_8 in the presence of an alkali halide, AX, into A_2NbX_6 and $A_4Nb_6X_{18}$. When the reaction is performed in niobium tubes or in the presence of niobium metal, it goes over into an outright reduction of the Nb_3X_8 to $A_4Nb_6X_{18}$.^{12,13} A disadvantage of this method is the use of Nb_3X_8 , which has to be prepared from NbX_5 .

The conproportionation of niobium pentachloride with niobium metal has been accomplished previously, by McCarley and coworkers.^{11,12} Niobium pentachloride, niobium metal, and excess potassium chloride were reacted for 4-5 days in electron beam sealed niobium tubes to yield $K_4Nb_6Cl_{18}$ and later¹⁴ the same procedure was used to produce $Li_4Nb_6Cl_{18}$. However, the drawbacks of this method are long reaction time, incomplete reduction of niobium pentachloride, and the apparent need for electron beam sealed niobium tubes.

Coordination Compounds Based on $(M_6X_{12})^{n+}$ Cluster Cations

McCarley, Hughes, Cotton, and Zimmerman¹⁵ in 1965, and Espenson and McCarley¹⁶ in 1966, established that $(M_6X_{12})^{2+}$ cluster cations in solution may undergo one and two electron oxidation, and subsequently a variety of coordination compounds containing M_6X_{12} cations in the oxidation states +2, +3, and +4 were synthesized.

Anionic halide complexes of the general formula $A_n[(M_6X_{12})Y_6]$ (A=univalent cation; n=2, 3; M=Nb, Ta; X=Cl, Br; Y=F, Cl, Br, I) have been prepared by McCarley's group,^{14,17} by Mackay and Schneider,¹⁸ by Spreckelmeyer¹⁹ and by Schäfer's group.²⁰ Ethanolic solutions of the appropriate hydrates, $M_6X_{14} \cdot 8H_2O$ were saturated with hydrogen halide HY, and after oxidation of the cluster the complex was precipitated by the addition of an excess of the halide, AY.

A series of complexes $[(Nb_6Cl_{12})Cl_2L_4]$ with oxygen

donor ligands, L, was reported by Field and Kepert.²¹ To obtain the pyridine-N-oxide, triphenylphosphine oxide, and triphenylarsine oxide complexes, ethanolic solutions of $\text{Nb}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$ and of the particular ligand, L, were mixed and the resultant mixture if necessary, evaporated. Complexes with the ligands dimethylsulphoxide, and dimethylformamide were precipitated by heating a solution of $\text{Nb}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$ in the liquid ligand with a small volume of isopropanol.

Boorman and Straughan²² claimed the preparation of a pyridine adduct, $(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 12\text{C}_5\text{H}_5\text{N}$. Substituted hydrates $(\text{Nb}_6\text{Cl}_{12})\text{X}_2 \cdot n\text{H}_2\text{O}$ (X=F, Br) and $(\text{Nb}_6\text{Br}_{12})\text{Cl}_2 \cdot n\text{H}_2\text{O}$ were synthesized by Boorman and Straughan²² and by McCarley's group.¹⁴

Structure and Bonding

Vaughan, Sturdivant, and Pauling,¹ in 1950 found by investigations of diffuse X-ray scattering of alcoholic solutions of $\text{Ta}_6\text{Cl}_{14}$, $\text{Ta}_6\text{Br}_{14}$, and $\text{Nb}_6\text{Cl}_{14}$ that the $(\text{M}_6\text{X}_{12})^{2+}$ cation consists of an M_6 octahedron with twelve halogens bridging over the octahedral edges. Their work has subsequently been confirmed by crystal structure investigations of solid $\text{Nb}_6\text{Cl}_{14}$,²³ $\text{Ta}_6\text{Cl}_{15}$,²⁴ Nb_6F_{15} ,²⁵ $\text{K}_4\text{Nb}_6\text{Cl}_{18}$,²⁶ $[(\text{CH}_3)_4\text{N}]_2(\text{Nb}_6\text{Cl}_{18})$,³ $[(\text{CH}_3)_4\text{N}]_3(\text{Nb}_6\text{Cl}_{18})$,²⁷ $\text{H}_2\text{Ta}_6\text{Cl}_{18} \cdot 6\text{H}_2\text{O}$,²⁸ Ta_6I_{14} ,²⁹ and $\text{Ta}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$.³⁰

If electron pair metal-metal bonds are considered to lie along each of the octahedral edges of an $(\text{M}_6\text{X}_{12})^{2+}$ cation, 24 bonding electrons would be required. However,

with the metal being niobium or tantalum, only 16 electrons are available for metal-metal bonding. Several molecular orbital approaches have been suggested to explain the bonding in the electron-deficient cluster cations. Cotton and Haas⁵ for example, combined d_z^2 , d_{xy} , d_{xz} , and d_{yz} atomic orbitals of all six metal atoms, to form eight bonding and sixteen antibonding molecular orbitals.

Magnetic susceptibility measurements made by McCarley's group,^{17,31} by Mackay and Schneider,¹⁸ and by Spreckelmeyer³² have shown the presence of one unpaired electron in $(M_6X_{12})^{3+}$ units and of no unpaired electrons in $(M_6X_{12})^{2+}$ and $(M_6X_{12})^{4+}$. These results were also corroborated by electron spin resonance measurements made by Mackay and Schneider¹⁸ which demonstrated that the unpaired electron, in the $(M_6X_{12})^{3+}$ unit, occupies an orbital singlet level, which because of strong hyperfine interaction equally with all six metal atoms, is a molecular orbital centered primarily on the octahedron of metal atoms. Converse's and McCarley's work³¹ further indicated electron delocalization and exchange coupling between cluster units via the bridging atoms.

All these experiments have shown the highest occupied molecular orbital to be of an A-type symmetry. However, no definite experimental evidence has been reported so far concerning the arrangements of the other occupied molecular orbitals.

CHAPTER III

EXPERIMENTAL

Niobium pentachloride and some of the other starting materials needed for the syntheses are sensitive to atmospheric moisture. Therefore the majority of the experimental work was done under a dry nitrogen atmosphere or in evacuated glass systems. Materials were handled in a dry box under an atmosphere of nitrogen which had been passed over Linde 4A Molecular Sieves. An adequate supply of exposed phosphorus pentoxide was kept in the dry box at all times.

Materials

Niobium metal was used in the form of high purity pellets from E. I. duPont de Nemours and Company.

Niobium pentachloride of 99.5% purity was supplied by Research Organic/Inorganic Chemical Company. It was stored inside the dry box.

Anhydrous aluminum chloride of 99.5% purity, obtained from Research Organic/Inorganic Chemical Company, was also stored in the dry box.

All other reagents and solvents were rather common chemicals. They all were of reagent grade quality.

Synthesis

Reduction of Niobium Pentachloride in Molten Halides

Various attempts were made to use as reaction media molten salt mixtures under atmospheric pressure.

Reduction with Aluminum Metal in Ammonium Chloride/ Aluminum Chloride Mixtures

Inside a dry box, 15.0 g (55.5 mmoles) of niobium pentachloride, 10.0g (370 mmoles) of aluminum filings, 13.4 g (84 mmoles) of ammonium chloride, and 33.3 g (250 mmoles) of anhydrous aluminum chloride were ground together and placed in a 100 ml tapered round bottom flask, which was subsequently fitted with a stopcock and a balloon containing dry nitrogen. The flask was heated gradually with a heating mantle equipped with an iron-constantan thermocouple. At a temperature of 220°C, the balloon burst, probably due to the evaporation of some of the niobium pentachloride into the balloon.

Reduction with Aluminum Metal in a Sodium Chloride/ Aluminum Chloride Melt

Inside a dry box, 10.0 g (37 mmoles) of niobium pentachloride, 15.0 g (555 mmoles) of aluminum filings, 11.7 g (200 mmoles) of sodium chloride, and 39.8 g (298 mmoles) of anhydrous aluminum chloride were ground together and placed in a 100 ml tapered round bottom flask containing a magnetic stirring bar. Then the flask was fitted with a stopcock and a balloon containing dry nitrogen, and it was placed in a heating mantle on top of

a magnetic stirrer. During two days it was gradually and under stirring brought to a temperature of 190°C . The liquid mixture was kept at this temperature for one more day and then, during three days, brought slowly up to a maximum temperature of 370°C . After 5 minutes the balloon and the stopcock were removed, and the liquid was poured onto a sheet of aluminum foil. A black-gray colored solid was obtained. However, when it was dissolved in water, a green solution indicating the presence of $(\text{Nb}_6\text{Cl}_{12})^{2+}$ material did not result.

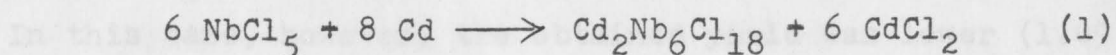
Reduction with Cadmium Metal in a Sodium Chloride/
Aluminum Chloride Melt

Inside a dry box, 10.0 g (89 mmoles) of mossy cadmium, 10.0 g (37 mmoles) of niobium pentachloride, 13.2 g (226 mmoles) of sodium chloride, and 36.4 g (274 mmoles) of anhydrous aluminum chloride were ground together and were placed in a tapered 100 ml round bottom flask. After the flask had been equipped in the same way as in the previous experiment, the mixture was heated as described above. A solution of the obtained product in water did not show the characteristic green color indicating the presence of $(\text{Nb}_6\text{Cl}_{12})^{2+}$ material.

Reduction of Niobium Pentachloride in a Water
Aspirator Vacuum

Attempts were made to synthesize $(\text{Nb}_6\text{Cl}_{12})^{2+}$ containing material by reduction of niobium pentachloride with various metals in a quartz tube under a water aspirator vacuum. This is essentially the method given

by Harned et al.,⁹ who used cadmium metal as the reducing agent according to:



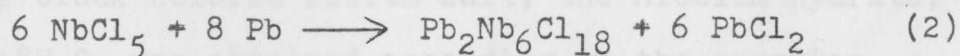
Reduction with Cadmium Metal

A ground mixture of 10.0 g (89 mmoles) of mossy cadmium and 16.2 g (60 mmoles) of niobium pentachloride was transferred into a tapered quartz tube of the dimensions 28x450 mm, which had been fitted with a tapered stopcock and a vacuum hose so that a water aspirator vacuum could be applied during heating. The tube was attached in an almost horizontal position, and the mixture was carefully heated with a Fisher burner proceeding from the open end toward the closed end. After the initial reaction was completed, the entire tube was heated for three hours to a bright red heat by means of three Fisher burners. The reaction product was dissolved in 700 ml of water. The obtained solution was acidified with 10 ml of concentrated hydrochloric acid and heated to boiling. After standing overnight, a green solution had resulted indicating the presence of $(\text{Nb}_6\text{Cl}_{12})^{2+}$ containing material. The green solution was filtered through a Büchner funnel and 1400 ml of concentrated hydrochloric acid was added until precipitation was complete as evidenced by a nearly colorless solution. The precipitate of $(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ was filtered through a frit and washed with concentrated hydrochloric acid and ether. It was then dried in vacuo over phosphorus pentoxide. The yield was 2.57 g (21.4%).

In a variation of this method, 2.5 g (43 mmoles) of sodium chloride was added to the initial reaction mixture. In this case, however, the obtained yield was lower (1.09 g, 9.1%).

Reduction with Lead Metal

Attempts were made to use lead metal to reduce niobium pentachloride to $(\text{Nb}_6\text{Cl}_{12})^{2+}$ containing material according to the equation:



A mixture of 16.2 g (60 mmoles) of niobium pentachloride and 17.0 g (82 mmoles) of fine lead filings were ground together and placed in a quartz tube. A water aspirator vacuum was applied and the tube was heated gradually with a Fisher burner for 45 minutes. Thereafter it was placed in a Lindberg tube furnace for three hours and heated gradually to a temperature of 800°C. The black colored product was dissolved in water. However, a green solution indicating the formation of $(\text{Nb}_6\text{Cl}_{12})^{2+}$ material did not result. Another attempt was made using lead, but the heating was done with Fisher burners for two hours. No green solution was obtained.

Reduction with Tin Metal

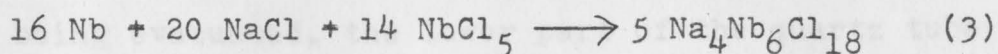
Niobium pentachloride was reduced as noted previously except that tin was used as the reducing agent.

A ground mixture of 10.0 g (84 mmoles) of tin filings and 16.2 g (60 mmoles) of niobium pentachloride was placed in a quartz tube and heated gradually with Fisher

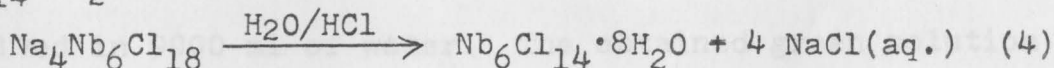
burners for three hours. The product was dissolved in water, acidified with 10 ml of concentrated hydrochloric acid and heated. No green solution was obtained.

High-Temperature Conproportionation of Niobium Metal in the Presence of Sodium Chloride

Various experimental arrangements were used to reduce niobium pentachloride according to the equation:



From the black colored sodium salt, the niobium hydrate, $\text{Nb}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$ was obtained according to the equation:



Reaction in an Aspirator Vacuum

Inside a dry box, 7.0 g (120 mmoles) of sodium chloride, 14.0 g (52 mmoles) of niobium pentachloride and 18.0 g (194 mmoles) of niobium pellets were ground together. The mixture was placed in a quartz tube and heated in a similar way as described above for the reaction with cadmium metal. The blackish-brown colored product was dissolved in 300 ml of water, and a green solution indicating the presence of $(\text{Nb}_6\text{Cl}_{12})^{2+}$ containing material resulted. After filtering the solution, 1500 ml of concentrated hydrochloric acid was added until precipitation was completed. The precipitate was filtered through a frit and washed with concentrated hydrochloric acid and ether. It was dried in vacuo over phosphorus pentoxide. The yield was 0.83 g (3.7%).

Reaction in a Niobium Tube

Inside a dry box, 12.4 g (46 mmoles) of niobium pentachloride, 3.8 g (65 mmoles) of sodium chloride and 16.0 g (172 mmoles) of niobium metal pellets were ground together and placed in a niobium tube of the dimensions 19x80 mm. The tube was fitted with a niobium lid and transferred into the quartz tube described previously. After being evacuated, the lower part of the quartz tube was placed in a tube furnace and, within 15 days, gradually brought to a temperature of 900°C. The product was dissolved in 9000 ml of water. The obtained green solution was filtered and 9000 ml of concentrated hydrochloric acid was added until precipitation of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ was completed. The black precipitate was washed with concentrated hydrochloric acid and ether and dried in vacuo over phosphorus pentoxide. The yield was 8.00 g (40.8%).

In this first preparation, which was run under vacuum, a large amount of niobium pentachloride had sublimed into the cooler parts of the quartz tube before it could be either complexed by sodium chloride or reduced by the niobium metal. Therefore the reaction was run for a second time under an atmosphere of dry argon. After the niobium tube had been filled with the reactants and placed into the quartz tube as described above, the quartz tube was evacuated and fitted with a balloon containing dry argon. After heating in a tube furnace for 21 days to a maximum temperature of 950°C, it was found that the niobium tube had disintegrated. When the product was dissolved in

water no green solution indicating the presence of $(\text{Nb}_6\text{Cl}_{12})^{2+}$ containing material resulted.

Reaction in a Vacuum Sealed Vycor Tube

A Vycor tube fitted with a stopcock by means of a vacuum hose as shown in Figure 1 was evacuated and heated with a Bunsen burner to ensure complete removal of any moisture. The evacuated tube was brought into the dry box and filled with an intimately ground mixture of 11.7 g (200 mmoles) of sodium chloride, 37.8 g (140 mmoles) of niobium pentachloride and 60.0 g (650 mmoles) of niobium metal pellets. The tube with its contents was then evacuated, sealed by means of an oxygen torch, and shaken for several minutes to thoroughly mix the reactants. It was then placed in a tube furnace. Within 6-8 hours, it was heated to a temperature of 850°C and left at this temperature overnight. The obtained $\text{Na}_4\text{Nb}_6\text{Cl}_{18}$ was successively extracted four times with 2000 ml portions of 0.01 M hydrochloric acid. After filtering, the intensely green solutions were treated with approximately equal volumes of concentrated hydrochloric acid and heated under stirring until precipitation of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ was completed. The black product was filtered through a frit, washed with concentrated hydrochloric acid and ether and dried in vacuo over phosphorus pentoxide. The yield was 55.3 g (92.0%). Part of the product was purified by dissolving it in a small volume of methanol. The filtered methanolic solution was added dropwise and under stirring to a large volume of

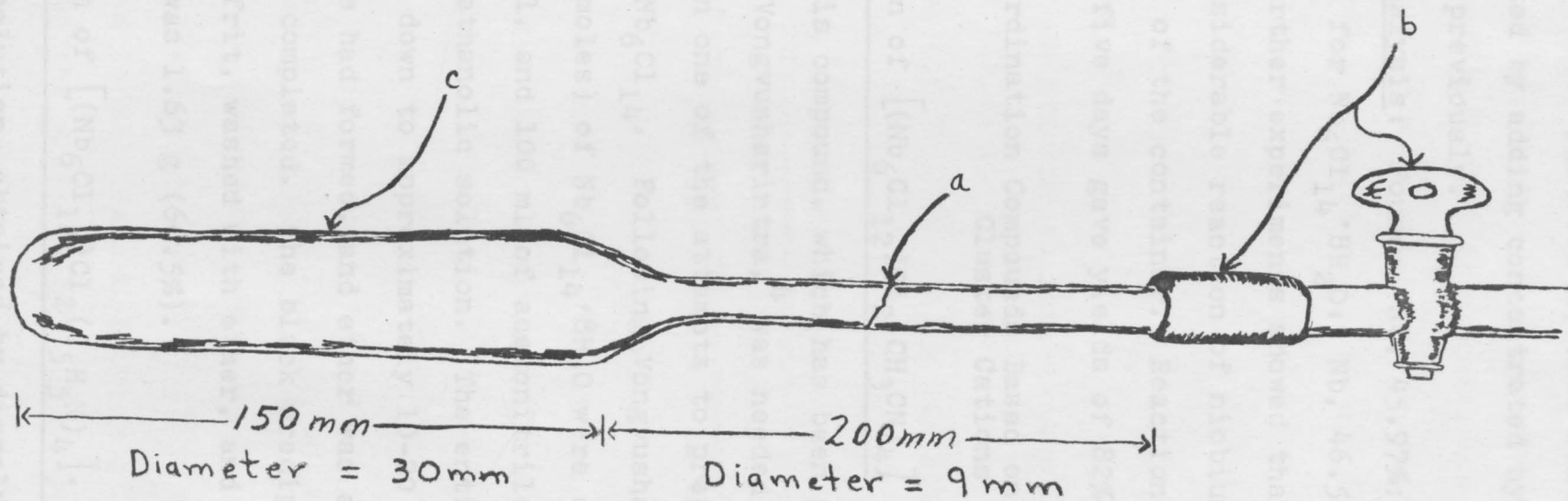


Figure 1. Vycor Reaction Vessel for Preparation of $\text{Na}_4\text{Nb}_6\text{Cl}_{18}$

- a. Point of sealing
- b. Vacuum hose and stopcock
- c. Reaction chamber

water. From the filtered aqueous solution the hydrate was precipitated by adding concentrated hydrochloric acid as described previously.

Analysis: Found: Nb, 45.97%; Cl, 41.22%.

Calculated for $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$: Nb, 46.53%; Cl, 41.43%.

Further experiments showed that prolonged heating caused considerable reaction of niobium metal with the glass wall of the container. Reaction mixtures heated for three and five days gave yields of 82% and 72% respectively.

Coordination Compounds Based on $(\text{Nb}_6\text{Cl}_{12})^{n+}$
Cluster Cations

Preparation of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{CH}_3\text{CN})_4]$

This compound, which has been prepared and described before by Vongvusharintra,⁴ was needed as a starting material in one of the attempts to prepare the pyridine adduct of $\text{Nb}_6\text{Cl}_{14}$. Following Vongvusharintra's procedure, 2.4 g (2 mmoles) of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ were dissolved in 100 ml of methanol, and 100 ml of acetonitrile was added to the filtered methanolic solution. The entire solution was evaporated down to approximately 10-20 ml. A black precipitate had formed, and ether was added until precipitation was completed. The black precipitate was filtered through a frit, washed with ether, and dried in vacuo. The yield was 1.63 g (66.5%).

Preparation of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_4]\cdot 1.5\text{C}_5\text{H}_5\text{N}$

A solution, obtained by dissolving 0.6 g (0.5 mmoles)

of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ in 60 ml of hot pyridine, was filtered and then evaporated to one-third of its original volume. The black precipitate that had formed was filtered through a frit and washed with pyridine, a 1:1 mixture of pyridine and methanol, and methanol. It was then dried in vacuo over phosphorus pentoxide. The yield was 0.36 g (48.0%).

Analysis: Found: Nb, 38.05%; Cl, 33.23%; Cl:Nb, 13.73:6.00. Calculated for $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_4]\cdot 1.5\text{C}_5\text{H}_5\text{N}$: Nb, 37.44%; Cl, 33.33%.

In an attempt to replace $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ as the starting material by the acetonitrile adduct, 1.63 g (1.3 mmoles) of $\text{Nb}_6\text{Cl}_{14}\cdot 4\text{CH}_3\text{CN}$ was dissolved in 700 ml of pyridine under heating and stirring. The resulting solution was filtered while hot, and evaporated to three-sevenths of its original volume. The obtained brownish-black micro-crystalline product was filtered through a frit and washed with ether, a 1:1 mixture of ethanol and pyridine, ethanol, and ether. It was dried in vacuo over sodium hydroxide for thirty minutes. The yield was 1.24 g (62.3%).

Analysis: Found: Nb, 38.14%; Cl, 32.55%; Cl:Nb, 13.42:6.00.

Preparation of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{C}_2\text{H}_5\text{CN})_4]$

In an attempt to prepare the propionitrile adduct of $\text{Nb}_6\text{Cl}_{14}$, 0.58 g (0.5 mmoles) of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ were dissolved in 25 ml of methanol, and 25 ml of propionitrile was added to the filtered solution. The resulting solution was evaporated on a hot plate to one-fifth of its original

volume. While the solution was still hot, ether was added until precipitation was completed. The green colored precipitate was filtered through a frit and washed with ether. It was dried by passing air through it. The yield was 0.53 g (85.5%).

Analysis: Found: Nb, 43.31%; Cl, 36.85%; Cl:Nb, 13.30:6.00. Calculated for $(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{C}_2\text{H}_5\text{CN})_4$: Nb, 43.76%; Cl, 38.95%.

Preparation of $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]$

In an attempt to prepare $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]$, 2.4 g (2 mmoles) of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ were dissolved in 100 ml of ethanol. During one hundred minutes, the resulting solution was saturated with hydrogen bromide gas, and 16.0 g (104 mmoles) of dry tetramethylammonium bromide was added. The obtained precipitate, probably close in composition to $[(\text{CH}_3)_4\text{N}]_4[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]$, was filtered through a frit and washed with ethanol, a 3:1 mixture of ethanol and chloroform, and with chloroform. A sample of this product (0.80 g, 0.45 mmoles) was dissolved in 30 ml of ethanol. After the ethanolic solution was saturated with dry gaseous hydrogen bromide, 0.10 g (0.4 mmoles) of iodine and 2.7 g (17.5 mmoles) of dry tetramethylammonium bromide were added with stirring. The needle-shaped precipitate was filtered and washed as described above. It was dried in vacuo over phosphorus pentoxide.

Analysis: Found: Nb, 34.99%; halogen as Cl, 40.28%; halogen:Nb. 18.07:6.00. Calculated for

$[(CH_3)_4N]_2[(Nb_6Cl_{12})Br_6]$; Nb, 34.62%; halogen as Cl, 39.63%.

Niobium

Niobium was determined gravimetrically as the oxide, Nb_2O_5 . Samples were weighed directly into tared crucibles, oxidized with concentrated nitric acid, dried and ignited.¹¹

Halogens

Halogen was determined by potentiometric titration with standard silver nitrate solution. The samples were decomposed with dilute sodium hydroxide solution and hydrogen peroxide. The obtained solutions were acidified with concentrated nitric acid and titrated with silver nitrate solution.³³

Physical Measurements

X-Ray Diffraction

X-ray diffraction data were obtained with a 114.59mm Debye-Scherrer powder camera. Finely powdered samples were packed and hermetically sealed in 0.2mm Lindemann glass capillaries. These were exposed to Ni-filtered $Cu K\alpha$ radiation. Exposure time varied from 24-50 hours depending on the sample.³⁴

Analytical Procedures

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CHAPTER IV

RESULTS AND DISCUSSION

Synthesis of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$

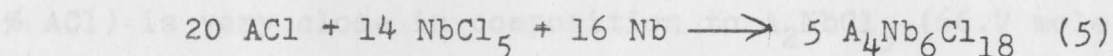
All methods used for the preparation of $\text{Nb}_6\text{Cl}_{14}\cdot 8\text{H}_2\text{O}$ involved a high-temperature synthesis of $(\text{Nb}_6\text{Cl}_{12})^{2+}$ containing material. This material was extracted and, from the purified aqueous solution, the hydrate was precipitated.

Reductions of niobium pentachloride in molten salt mixtures were attempted under atmospheric pressure to allow for a greater experimental simplicity. They all were unsuccessful. In one case, the niobium pentachloride sublimed before the ammonium chloride/aluminum chloride mixture became a liquid. In the other cases, some reduction apparently took place, however no $(\text{Nb}_6\text{Cl}_{12})^{2+}$ material could be extracted from the reaction product. This was probably due to the temperature not being high enough.

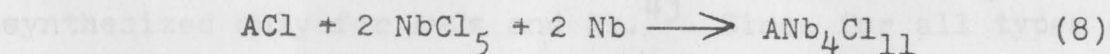
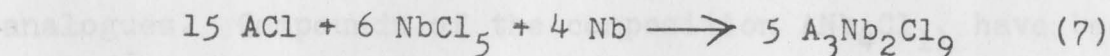
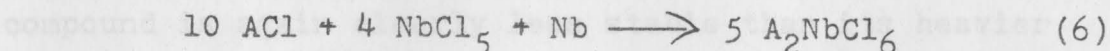
Harned's method⁹ involving the reduction of niobium pentachloride in an aspirator vacuum did not work with lead or tin as the reducing agent. Only the product of cadmium reaction gave the characteristic green, $(\text{Nb}_6\text{Cl}_{12})^{2+}$ containing solution. It is however quite possible that in the reduction with lead metal, $(\text{Nb}_6\text{Cl}_{12})^{2+}$ clusters were formed and immediately complexed to form $\text{Pb}_2\text{Nb}_6\text{Cl}_{18}$. The Pb^{2+} ion has approximately the same ionic radius as the Ba^{2+} ion, and the compound $\text{Ba}_2\text{Nb}_6\text{Cl}_{18}$ ^{35,36} is known to be insoluble in water and very stable.

In comparison with the other methods attempted, the conproportionation of niobium pentachloride with niobium metal has several distinct advantages. First, even with low yields it will supply rather large amounts of cluster material, since both the oxidizing and the reducing agents are transformed into the desired product. Second, since the reducing agent is niobium metal, an excess of it cannot overreduce the pentachloride to the metal. Third, this method does not use a molten salt as a solvent, and therefore upon extraction with water does not introduce large amounts of foreign substances into the aqueous solution.

The formation of $(\text{Nb}_6\text{Cl}_{12})^{2+}$ cluster material in a high-temperature synthesis is facilitated if the cluster cation is stabilized, by complexation, into an $(\text{Nb}_6\text{Cl}_{18})^{4-}$ anion. This was accomplished by the addition of an alkali chloride according to the equation:



This reaction needs an alkali chloride/niobium pentachloride ratio of 10:7. It can be assumed to be in competition with the reactions:



which need alkali chloride/niobium pentachloride ratios of 5:2, 5:2, and 1:2 respectively. To favor the formation of $\text{A}_4\text{Nb}_6\text{Cl}_{18}$, only the stoichiometric alkali chloride/niobium

pentachloride ratio given by equation (5) was used.

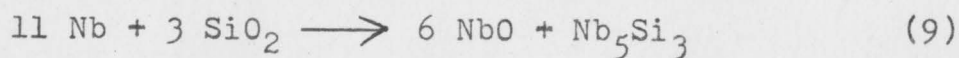
Of great importance for the success of reaction (5) is the selection of the alkali chloride, ACl, since the relative stabilities of the compounds A_2NbCl_6 , $A_3Nb_2Cl_9$, and ANb_4Cl_{11} competing with $A_4Nb_6Cl_{18}$ are functions of the particular alkali ion, A.

In the systems ACl-NbCl₄,^{37,38} Na₂NbCl₆ melts at 582°C, its heavier analogues K₂NbCl₆, Rb₂NbCl₆, and Cs₂NbCl₆ at 782, 802, and 822°C. The alkali chlorides NaCl, KCl, RbCl, and CsCl have melting points of 801, 776, 715, and 646°C, respectively. According to general considerations made by Wagner,³⁹ this pattern can be interpreted as indicating a clearly lower stability for Na₂NbCl₆. Of the species $A_3Nb_2Cl_9$, only Cs₃Nb₂Cl₉⁴⁰ has been thoroughly investigated so far. However, in the systems ACl-NbCl₃, compounds A_2NbCl_5 have been reported^{41,42} as the only occurring double salts. Since $A_3Nb_2Cl_9$ (60 mole % ACl) is very close in composition to A_2NbCl_5 (66.7 mole % ACl) and since the maxima in the phase diagrams are rather broad, the reported species might very well be of the type $A_3Nb_2Cl_9$. As indicated by the melting points, the sodium compound is again clearly less stable than its heavier analogues. Compounds of the composition ANb_4Cl_{11} have been synthesized only for A=Cs and Rb.⁴³ Since for all types of compounds competing with $A_4Nb_6Cl_{18}$ the sodium representatives have remarkably lower stabilities than their heavier analogues, sodium chloride was selected as the complexing agent.

In addition to stabilizing the $(\text{Nb}_6\text{Cl}_{12})^{2+}$ cation as an $(\text{Nb}_6\text{Cl}_{18})^{4-}$ complex anion, the added sodium chloride serves another purpose. In the initial stages of the reaction it complexes volatile niobium pentachloride to non-volatile sodium hexachloroniobate (V). This is of special importance for reactions run in sealed Vycor tubes. Niobium pentachloride reaches its critical point at 534°C and 46 atmospheres of pressure,⁴⁴ and with 0.14 moles of niobium pentachloride confined to a volume of 60 ml, the pressure could easily exceed 150 atmospheres at 550°C .

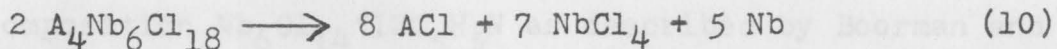
The formation of sodium hexachloroniobate (V), that prevents the build-up of an excessive pressure of niobium pentachloride, seems to go to completion only under somewhat elevated pressure and in tubes that are sealed and can be heated in their entirety. In reactions run in an aspirator vacuum or at atmospheric pressure, sizeable amounts of niobium pentachloride sublimed into the cooler part of the tube, even though the sodium chloride added according to equation (5) was more than sufficient to complex all of the niobium pentachloride.

Another factor essential for the success of reaction (5) is the use of a sufficient excess of niobium metal. This will favor the formation of $\text{A}_4\text{Nb}_6\text{X}_{18}$ which contains niobium in a lower oxidation state than the competing species A_2NbX_6 , $\text{A}_3\text{Nb}_2\text{X}_9$, and $\text{ANb}_4\text{X}_{11}$. It will also compensate for the loss of niobium due to reaction with the glass wall^{13,26} according to the equation:



Schäfer, who pointed this out, has also suggested that

$A_4M_6X_{18}$ may decompose according to the equation:



if heated in vacuo.^{13,26}

The apparent lack of excessive pressure in the initial stages of the reduction made it possible to minimize reactions (9) and (10) by using short reaction times and by "stuffing" the reaction tubes.

Coordination Compounds of $(Nb_6Cl_{12})^{n+}$ Cluster Cations

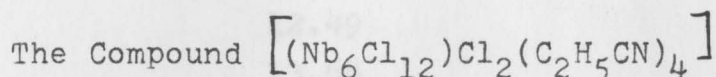
Pyridine Adduct of $(Nb_6Cl_{12})Cl_2$

The pyridine adduct consists of glittering black crystals having the shape of flattened octahedra. The material seemed to lose its luster after being exposed to the open air for two weeks. The compound was insoluble in acetonitrile, acetone, ethanol and water and soluble in dimethylsulfoxide, methanol, and pyridine.

According to the analysis, the pyridine adduct is very close in composition to $[(Nb_6Cl_{12})Cl_2 \cdot (C_5H_5N)_4] \cdot 1.5 (C_5H_5N)$, however, it is quite possible that the correct composition of the compound is $[(Nb_6Cl_{12})Cl_2 \cdot (C_5H_5N)_4] \cdot 2(C_5H_5N)$. Only four pyridine molecules are needed to complete the coordination sphere of the cluster. The remaining ones probably just fill empty space in the lattice, and half a molecule of pyridine per formula unit might very well be lost when the compound is exposed to a vacuum while being dried.

None of the attempts to prepare a pyridine adduct of $\text{Nb}_6\text{Cl}_{14}$ however, supplied a product of or close to the composition $\text{Nb}_6\text{Cl}_{14} \cdot 12\text{C}_5\text{H}_5\text{N}$ as described by Boorman and Straughan.²²

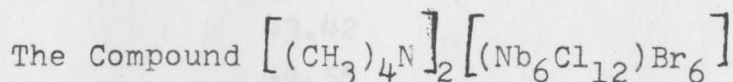
X-ray powder diffraction data for the pyridine adduct are given in Table 1.



As indicated by the low Cl:Nb ratio of 13.30:6.00, the propionitrile adduct was not obtained in a pure form. Apparently some cluster material decomposed when the solution was heated during the preparation.

The compound is insoluble in carbon tetrachloride, chloroform, and ether. The compound is soluble in methanol, ethanol, and iso-propanol. In water, propionitrile, and acetone, it is only slightly soluble.

X-ray powder diffraction data for the propionitrile adduct are given in Table 2.



The halogen:niobium ratio of 18.07:6.00, that has been found for this product by analysis, tends to confirm that all six sites at the $(\text{Nb}_6\text{Cl}_{12})^{4+}$ cation are occupied by halide terminal ligands.

used was $\text{CuK}\alpha$.

All intensities were estimated visually relative to a value of 10 for the most intense line.

TABLE 1
X-RAY DIFFRACTION DATA FOR PYRIDINE ADDUCT^a

Relative ^b intensity	2 θ , degrees	Observed "d" spacing, Å
10	8.07	10.955
8	9.14	9.6752
9	11.38	7.7753
5	12.49	7.0867
6	13.64	6.4917
6	15.82	5.6017
1	17.07	5.1942
2	19.10	4.6465
2	21.26	4.1790
1	23.01	3.8650
2	27.89	3.1988
2	30.00	2.9785
3	34.21	2.6210
1	37.42	2.4032
2	38.01	2.3672
1	39.09	2.3043
2	39.67	2.2719
2	41.67	2.1674
2	42.74	2.1156
2	43.42	2.0840
1	44.56	2.0333
4	48.88	1.8632
4	50.96	1.7919
3	56.46	1.6297
3	59.26	1.5593

^aExposure time for this pattern was 30 hours. Radiation used was CuK α .

^bAll intensities were estimated visually relative to a value of 10 for the most intense line.

TABLE 2
X-RAY DIFFRACTION DATA FOR PROPIONITRILE ADDUCT^a

Relative ^b intensity	2θ, degrees	Observed "d" spacing, Å
10	10.17	8.6975
8	11.02	8.0285
3	12.40	7.1379
5	20.24	4.3873
3	21.88	4.0620
4	23.43	3.7967
5	25.43	3.5024
5	29.05	3.0737
7	34.72	2.5836
1	36.49	2.4623
2	38.36	2.3464
6	40.65	2.2194
2	42.94	2.1062
2	47.77	1.9039
1	52.92	1.7301
4	56.50	1.6287
1	58.27	1.5834
1	59.55	1.5524
1	64.00	1.4547
1	64.91	1.4365

^aExposure time for this pattern was 50 hours. Radiation used was CuK α .

^bAll intensities were estimated visually relative to a value of 10 for the most intense line.

However, from the fact that both halogen and niobium are high it can be concluded that the product contains more chlorine and less bromine than indicated by the above formula, and its composition is probably close to $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Br}_{5.4}\text{Cl}_{0.6}]$.

Apparently, it is rather difficult to replace all chloride terminal ligands brought in by the starting material $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ by the larger bromide.

X-ray powder diffraction data for $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Br}_6]$ are given in Table 3.

^aExposure time for this pattern was 24 hours. Radiation used was $\text{Cu K}\alpha$.

^bAll intensities were estimated visually relative to a value of 10 for the most intense line.

TABLE 3

X-RAY DIFFRACTION DATA FOR $[(CH_3)_4N]_2[Nb_6Cl_{12}Br_6]^a$

Relative ^b intensity	2 θ , degrees	Observed "d" spacing, Å
7	8.36	10.5760
10	9.21	9.6018
5	10.12	8.7404
5	12.38	7.1494
8	13.73	6.4493
4	16.75	5.2927
5	18.51	4.7932
5	19.10	4.6465
6	20.31	4.3723
8	21.20	4.1907
6	26.69	3.3399
3	27.64	3.2272
4	27.97	3.1899
4	28.93	3.0862
4	29.77	3.0010
5	30.60	2.9214
5	31.35	2.8532
4	32.08	2.7900
4	33.83	2.6495
8	34.80	2.5779
3	37.64	2.3896
3	38.66	2.3289
8	39.67	2.2719
3	41.95	2.1536
4	42.39	2.1322
4	43.00	2.1034
4	44.49	2.0363
4	45.32	2.0009
4	48.68	1.8704
4	49.41	1.8445
6	50.49	1.8075
1	52.04	1.7573
4	58.61	1.5750

^aExposure time for this pattern was 24 hours. Radiation used was Cu K α .

^bAll intensities were estimated visually relative to a value of 10 for the most intense line.

CHAPTER V

SUGGESTIONS FOR FUTURE WORK

With an efficient synthesis of the hexanuclear niobium chloride hydrate available that has subsequently been applied to the preparation of the corresponding niobium bromide⁴ and of the analogous tantalum bromide and chloride,⁴⁵ investigations of coordination compounds based on M_6X_{12} central cations should no longer be hindered by the lack of starting materials.

Much work can be done now on the effect of terminal ligands on the structure of M_6X_{12} central cations. Single crystal X-ray studies could be undertaken to investigate distortions of M_6X_{12} units caused by mixed sets of terminal ligands or to investigate changes in bond distances and angles caused by the exchange of a complete set of terminal ligands. With exact values for bond distances and angles obtained from X-ray data, detailed molecular orbital calculations could be made in order to get a better understanding of the bonding in metal cluster compounds.

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