SYNTHESIS OF SOME HEXANUCLEAR NIOBIUM HALIDE CLUSTER COMPOUNDS

by

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ABSTRACT

SYNTHESIS OF SOME HEXANUCLEAR NIOBIUM HALIDE CLUSTER COMPOUNDS

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A fast, efficient, and inexpensive method was developed for the preparation of $Nb_6Br_{14} \cdot 8H_2O$. This compound is an important starting material for the preparation of coordination compounds based on hexanuclear $(Nb_6Br_{12})^{n+}$ central cations and was available previously only in minute quantities. Potassium bromide, niobium pentabromide, and excess niobium metal were conproportionated in Vycor tubes at 720°C to give $K_4Nb_6Br_{18}$, which upon extraction with water forms $Nb_6Br_{14} \cdot 8H_2O$ in yields up to 80%.

The new coordination compounds $\left[(Nb_6Cl_{12})Cl_2(CH_3CN)_4\right]$, $\left[(Nb_6Br_{12})Br_2(CH_3CN)_4\right]$, and $\left[(Nb_6Cl_{12})F_2(C_5H_5NO)_4\right]$ have been synthesized. In attempts to prepare the adducts, $(Nb_6Cl_{12})F_2L_4$ (L = CH_3CN, DMSO, DMF), impure or nonuniform products were obtained.

The new complex, $\left[(Nb_6Cl_{12})Cl_2\ (CH_3CN)_4\right]$, was used as a starting material for the preparation of a product $(Me_4N)_3\left[(Nb_6Cl_{12})Cl_6\right] \cdot 3CH_3CN$ with an analysed Cl:Nb ratio of 17.99:6.00. Anionic $\left[(Nb_6Cl_{12})Cl_6\right]^{n-}$ complexes with Cl:Nb ratios close to the ideal value of 18.00:6.00 are very difficult to obtain with $Nb_6Cl_{14} \cdot 8H_2O$ as starting material.

Attempts to dehydrate $Nb_6Cl_{14} \cdot 8H_2O$ with thionyl chloride caused its oxidation to $(Nb_6Cl_{12})^{4+}$-containing material. Impure Nb_6Cl_{16} adducts were formed. Reaction of $Nb_6Cl_{14} \cdot 8H_2O$ with thionyl chloride and acetonitrile did not lead to the adduct $Nb_6Cl_{16} \cdot 2CH_3CN$, but yielded impure $(Nb_6Cl_{12})^{4+}$-containing materials with approximate Cl:Nb ratios of 18:6 and 28:6, respectively.

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CHAPTER I

INTRODUCTION

Hydrated hexanuclear metal halides, $[(M_6X_{12})X_2(H_2O)_4] \cdot 4H_2O$ or $M_6X_{14} \cdot 8H_2O$ (M=Nb,Ta; X=Cl,Br), are the most common representatives of a particular class of coordination compounds that are based on $(M_6X_{12})^{n+}$ cluster units as central cations. $(M_6X_{12})^{n+}$ cluster cations consist of metal-metal bonded M_6 octahedra surrounded by twelve halogen atoms bridging over the octahedral edges.[1] Each metal atom has one site open for attachment of a terminal ligand, and negative, neutral, and positive complexes with the $(M_6X_{12})^{n+}$ cluster units in different oxidation states have been reported. Examples are $(Et_4N)_2[(Nb_6Cl_{12})Cl_6]$,[2] $[(Nb_6Cl_{12})Cl_2(C_5H_5NO)_4]$,[3] and $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$.[4]

Though compounds with metal-metal bonds have evoked great interest within the past decade, only a few crystal structure investigations have been done on complexes based on Nb_6X_{12} cluster cations. This is the result of the difficulty of preparation of these compounds.

First, the syntheses of these complexes are based on the use of the hydrates of the general formula $Nb_6X_{14} \cdot 8H_2O$ as starting materials. Since previous methods for the preparation of the hydrates have been time consuming and inefficient, these compounds have been available only in limited quantities.

Second, Nb_6X_{12} cluster cations in alcoholic solutions of the hydrates tend to decompose, probably due to reaction with water, leaving insoluble decomposition products. They also tend to exchange only part of their water molecules for other terminal ligands, and a number of anionic complexes $A_2[(Nb_6X_{12})X_6]$ reported in the literature have halogen:niobium ratios that are well below the theoretical ratio of 18.00:6.00. Pure, well-crystallized complexes are very difficult to obtain.

One possible way of avoiding difficulties caused by the presence of water would be to use acetonitrile adducts of hexanuclear niobium halides as starting material for the preparation of the desired products. So far, however, acetonitrile adducts of this kind have not been reported.

It was the purpose of this project to attempt to develop a fast, efficient, and inexpensive synthesis of $Nb_6Br_{14}\cdot 8H_2O$, and to attempt the preparation of pure, well-crystallized complexes of hexanuclear niobium halides, particularly with acetonitrile as terminal ligand.

CHAPTER II

REVIEW OF PREVIOUS WORK

Preparation of niobium cluster halides

The first preparation of a polynuclear niobium chloride was accomplished in 1913 by Harned[5] who reduced $NbCl_5$ with Na(Hg) at elevated temperatures. The crystals he obtained from aqueous solution after extracting the product were formulated as $(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$. Nearly fifty years later Harned et al[6] reported the preparation of the chloride and of the analogous bromide from products obtained by reduction of niobium pentahalides with cadmium in vacuo. Robin and Kuebler,[7] Allen and Sheldon,[8] Boorman and Straughan,[9] Mackay and Schneider,[10] and Spreckelmeyer[11] have used the same method, which supplies the Nb_6Br_{14} hydrate only in minute quantities. Investigations of Schäfer and Bauer on the analogous tantalum chloride[12] suggest that the hydrates contain eight rather than seven molecules of water.

McCarley and coworkers have investigated a number of other methods for the preparation of the hydrates. Each method reported is based on a high-temperature synthesis of (Nb_6X_{12})—containing material that is subsequently extracted with water. $Nb_6Br_{14} \cdot 8H_2O$ was obtained in up to 30% yield by aluminum reduction of niobium pentabromide[13] in a gradient of 350/280°C; LiCl/KCl melts were successfully used for the reduction of $NbCl_5$ with cadmium[13,14] and LiBr/KBr melts for the reduction of $NbBr_5$ with aluminum.[13,14] A third method worked out by McCarley's group is the high-temperature disproportionation of Nb_3X_8[13] into A_2NbX_6 and $A_4Nb_6X_{18}$ (X=Cl, Br) in presence of an alkali halide AX. When performed in niobium tubes or in the presence of niobium metal, this reaction goes over into an outright reduction of Nb_3X_8 to $A_4Nb_6X_{18}$.[14,15] When extracted with water, $A_4Nb_6X_{18}$ produces $Nb_6X_{14}\cdot 8H_2O$. McCarley and coworkers[13] also attempted conproportionation of $NbCl_5$ and Nb in the presence of excess KCl in electron-beam-sealed niobium tubes.

The only anhydrous binary halides known so far that are based on (Nb_6X_{12}) groups are $(Nb_6Cl_{12})Cl_2$[16] and $(Nb_6F_{12})F_3$[17], both snythesized by Schäfer's group. $(Nb_6Cl_{12})Cl_2$ was prepared by high-temperature equilibration of Nb_3Cl_8 and niobium, and $(Nb_6F_{12})F_3$ by high-temperature reduction of NbF_5 with niobium metal.

The substituted dihalide hydrates $(Nb_6Cl_{12})X_2\cdot nH_2O$ (X=F, Br) and $(Nb_6Br_{12})Cl_2\cdot nH_2O$ have been reported by Boorman and Straughan[9], and McCarley _et al_[13,14]. Field and Kepert[3] synthesized a series of complexes of the formula $[(Nb_6Cl_{12})Cl_2L_4]$ with oxygen donor ligands, L.

Oxidation of $(Nb_6Cl_{12})^{2+}$ and $(Ta_6X_{12})^{2+}$ units in solution was established by McCarley _et al_[18] and by Espenson and McCarley;[19] and subseqnently a number of anionic halogen complexes $A_n[(M_6X_{12})Y_6]$ (A=univalent cation; n=2,3,4; M=Nb, Ta; X=Cl, Br; Y=F, Cl, Br, I) have been reported, mainly by McCarley *et al*,[20] Mackay and Schneider,[10] Spreckelmeyer,[11] and Schäfer *et al.*[21]

Structure and bonding

Vaughan, Sturdivant and Pauling[1] have shown by diffuse X-ray scattering studies on concentrated ethanolic solutions of $Nb_6Cl_{14} \cdot 8H_2O$ and $Ta_6Cl_{14} \cdot 8H_2O$ that these halides contain discrete octahedra of metal atoms with 12 halogens bridging over the octahedral edges.

Single crystal X-ray studies by Schäfer demonstrated that $(Nb_6Cl_{12})Cl_{12}$[16] and the isostructural $(Ta_6I_{12})I_2$[22] contain tetragonally flattened M_6 units. Each M_6X_{12} cluster unit shares four terminal halogens with its neighbors. The remaining two terminal sites on each cluster unit are occupied by inner halogens from neighboring clusters, and the weaker bonding to their terminal ligands allows these two metal atoms to retract toward the center of the cluster unit.

In $(Nb_6F_{12})F_3$[17] and also in $K_4\left[(Nb_6Cl_{12})Cl_6\right]$[23] all terminal sites are occupied by equivalent halogen atoms, and the octahedral clusters have been found to be regular.

Koknat and McCarley[24,25] have shown by single crystal X-ray studies on $\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6\right]$ and $\left[(CH_3)_4N\right]_2\left[(Nb_6Cl_{12})Cl_6\right]$ that oxidation of the cluster unit causes metal-metal bond distances to increase and metal-terminal halogen bond distances to decrease.

Compounds based on $(M_6X_{12})^{2+}$ clusters (M=Nb, Ta; X=Cl, Br) are electron-deficient. To form electron pair metal-metal bonds along the octahedral edges, 24 electrons would be required. However, only 16 electrons are available.

Several molecular orbital approaches have been suggested to describe the bonding in these cluster units. Cotton and Haas,[26] for example, combine d_z2, d_{xz}, d_{yz}, and d_{xy} atomic orbitals in each of the metal atoms to form 8 bonding and 16 antibonding molecular orbitals.

Magnetic measurements 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 $(M_6X_{12})^{4+}$ units. Electron spin resonance measurements made by Mackay and Schneider[10] demonstrated that the unpaired electron in a $(Nb_6Cl_{12})^{3+}$ group is delocalized over the Nb_6 unit.

These experiments tend to confirm the molecular orbital approach and show that the highest occupied molecular orbital has an a-type symmetry. No definite experimental evidence has been reported so far concerning the arrangement of the other occupied molecular orbitals.

CHAPTER III

EXPERIMENTAL

Equipment

It was necessary to handle the starting materials for the preparation of $Nb_6Br_{14}\cdot 8H_2O$ in an inert nitrogen atmosphere inside of a dry-box. Sufficient drying of the nitrogen was obtained by passing the gas over Linde 4A Molecular Sieves. An adequate supply of exposed phosphorus pentoxide was maintained in the dry box.

High temperature reductions of niobium pentabromide were generally carried out in evacuated and sealed Pyrex or Vycor tubes after the necessary preliminary steps had been carried out in the dry box and on the vacuum manifold. The sealed reaction tubes were heated in a manually controlled, Lindberg hinged split tube furnace.

Materials

The niobium metal used in this work in form of high purity pellets was from E. I. Dupont de Nemours and Company. Its main impurity was 690 ppm Ta.

Anhydrous niobium pentabromide of 99.5% purity was obtained from Research Organic/Inorganic Chemical Corporation.

$Nb_6Cl_{14}\cdot 8H_2O$ was kindly made available by J. A. Parsons in this laboratory.

The potassium bromide needed for high-temperature reductions was dried prior to use by heating in vacuo.

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

Syntheses

Reactions providing the Nb_6Br_{12} unit:

Reduction of niobium pentabromide in ammonium bromide/aluminum bromide molten salt mixtures

$(Nb_6Br_{12})^{2+}$-containing material was obtained by aluminum reduction of niobium pentabromide in ammonium bromide/aluminum bromide melts according to the equation:

$$16Al + 18NbBr_5 \longrightarrow 3(Nb_6Br_{12})^{2+} + 10AlBr_3 + 6AlBr_4^- \qquad (1)$$

A 100ml round bottom flask was filled inside of a dry box with 66.8g (250 mmoles) of anhydrous aluminum bromide, 23.5g (240 mmoles) of ammonium bromide, 14.9g (30 mmoles) of niobium pentabromide, and 8.1g (300 mmoles) of aluminum filings. By means of a tapered adaptor the flask was connected with a balloon containing nitrogen as an inert gas. Using a heating mantle the reaction mixture was brought to 330°C and maintained at this temperature for two days. The product was extracted with 1500 ml of water. After 25.0g of solid sodium bromide was added to the filtered solution, it was slowly evaporated to approximately 1/10 of its volume. The precipitated $Nb_6Br_{14}\cdot 8H_2O$ was filtered over a frit, washed with concentrated hydrobromic acid and ether and dried in vacuo over phosphorus pentoxide. Yield: 1.56g = 18.5%.

Several attempts to increase the yield by changing the reaction temperature and/or the ammonium bromide/

aluminum bromide ratio were unsuccessful.

Reduction of niobium pentabromide in lithium bromide/potassium bromide eutectic mixtures

Using a method developed by Fleming,[14] niobium pentabromide was reduced by aluminum metal in a lithium bromide/potassium bromide eutectic mixture according to the equation:

$$16Al + 18NbBr_5 + 28KBr \longrightarrow 3K_4Nb_6Br_{18} + 16KAlBr_4 \quad (2)$$

A Pyrex reaction tube was filled with 9.7g (80 mmoles) of potassium bromide, 10.5g (120 mmoles) of lithium bromide, 9.85g (20 mmoles) of niobium pentabromide, and 5.0g (185 mmoles) of aluminum filings and sealed under vacuum. After shaking the tube for several minutes in order to thoroughly mix its contents, it was slowly heated to 360°C and maintained at this temperature for 15 hours. After cooling, the product was extracted with 400 ml of water. After adding 2.0g of solid ammonium bromide the filtrate was slowly evaporated nearly to dryness. The precipitated $Nb_6Br_{14}\cdot 8H_2O$ was washed with hydrobromic acid and ether and dried _in vacuo_ over phosphorus pentoxide. Yield: 0.5g = 8.3%.

Several attempts were made replacing aluminum metal in the above reaction by niobium metal, leaving all other conditions unchanged. None of these attempts was successful.

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Several attempts were made replacing aluminum metal in the above reaction by niobium metal, leaving all other conditions unchanged. None of these attempts was successful.

High temperature conproportionation of niobium metal and niobium pentabromide in presence of potassium bromide

Niobium pentabromide was reduced with niobium metal according to the reaction

$$20KBr + 14NbBr_5 + 16Nb \longrightarrow 5K_4Nb_6Br_{18} \qquad (3)$$

An intimate mixture of 13.8g (28 mmoles) of $NbBr_5$ and 4.75g (40 mmoles) of KBr, to which 15g (160 mmoles) of niobium pellets was added, was sealed under vacuum in a Vycor tube. The reaction tube was shaken for several minutes to ensure thorough mixing of the reactants. During a period of 6-8 hours it was gradually brought up to 720°C and left at this temperature for 15 hours. After cooling, the product was extracted with 1000 ml of warm water with stirring. The dark green solution was filtered and treated with an equal volume of concentrated hydrobromic acid with stirring until precipitation was complete. The black product was washed with concentrated hydrobromic acid and ether and dried <u>in vacuo</u> over phosphorus pentoxide. Yield: 14.80g = 81.3%.

Analysis: Found: Nb, 30.16%; Br, 60.32%; Br:Nb, 13.95:6.00. Calculated for $Nb_6Br_{14}\cdot 8H_2O$: Nb, 30.62%; Br, 61.46%.

Unsuccessful attempts were made to further purify the product by dissolving 5.0g of it in 30 ml of methanol. The filtered methanolic solution was added dropwise with stirring to 500 ml of water. The hydrate was precipitated with concentrated hydrobromic acid from the filtered aqueous solution in the same way as described above.

Analysis: Found: for the purified hydrate $Nb_6Br_{14}\cdot 8H_2O$: Nb, 31.10%; Br, 60.81%; Br:Nb, 13.64:6.00.

Coordination compounds based on (Nb_6X_{12}) cations

$\left[(Nb_6Br_{12})Br_2\ (CH_3CN)_4\right]$

75 ml of acetonitrile was added to a filtered solution containing 1.0g of $Nb_6Br_{14}\cdot 8H_2O$ in 75 ml of methanol. The resulting acetonitrile solution was evaporated to 1/2 of its volume and allowed to cool down. The glittering black microcrystalline precipitate was filtered over a frit, washed with ether and dried *in vacuo* over phosphorus pentoxide.

Analysis: Found: Nb, 29.80%; Br, 57.45%; Br:Nb, 13.45:6.00. Calculated for $\left[(Nb_6Br_{12})Br_2(CH_3CN)_4\right]$: Nb, 30.29%; Br, 60.78%.

$\left[(Nb_6Cl_{12})Cl_2\ (CH_3CN)_4\right]$

A filtered solution containing 1.5g of $Nb_6Cl_{14}\cdot 8H_2O$ in 75 ml of methanol, to which 75 ml of acetonitrile had been added, was heated with stirring until it evaporated to about 25 ml. After cooling, the dark solution was filtered to yield olive colored decomposition products, then the solution was allowed to stand for two days until the solvent evaporated. To remove any acetamide which might have been formed in the reaction, the black crystalline material which remained was covered with 50 ml of chloroform. After two days of standing, 1.11 g of the product was isolated by filtration through a glass frit, washed with ether and dried in vacuo over phosphorus pentoxide.

Analysis: Found: Nb, 45.26%; Cl, 40.36%; Cl:Nb, 14.02:6.00; N, 4.37%. Calculated for $[(Nb_6Cl_{12})Cl_2(CH_3CN)_4]$: Nb, 45.77%; Cl, 40.75%; N, 4.60%.

$(Nb_6Cl_{12})F_2 \cdot 9H_2O$

This compound was prepared using a method developed by Fleming.[14] A filtered solution containing 1.2g (1 mmole) of $Nb_6Cl_{14} \cdot 8H_2O$ in 10 ml of methanol was added dropwise at a slow rate and with stirring to 300 ml of water contained in a plastic beaker. The solution was made approximately 0.6M in hydrofluoric acid by adding 6 ml of 48% hydrofluoric acid, and placed on a boiling water bath until all but 10 ml of the solvent evaporated. The solution became nearly colorless, and black hexagonal needles crystallized on the bottom of the plastic beaker. The product was collected on a filter paper in a plastic Buechner funnel, washed with ether and dried in vacuo over phorphorus pentoxide.

Analysis: Found: Nb, 46.72%; Cl, 35.70%; Cl:Nb, 12.01:6.00. Calculated for $(Nb_6Cl_{12})F_2 \cdot 9H_2O$: Nb, 47.12%; Cl, 35.95%.

Acetonitrile adduct of $(Nb_6Cl_{12})F_2$

Methanolic solutions of $(Nb_6Cl_{12})F_2 \cdot 9H_2O$ were treated with acetonitrile in ways similar to those described for the preparation of $Nb_6Cl_{14}\cdot 4CH_3CN$ and $Nb_6Br_{14}\cdot 4CH_3CN$. Two different non-uniform products were obtained.

Analysis: Found: Product 1: Cl, 33.16%. Product 2: Cl, 32.68%. Calculated for $\left[(Nb_6Cl_{12})F_2\ (CH_3CN)_4\right]$: Cl, 35.90%.

$\left[(Nb_6Cl_{12})F_2\ (DMSO)_4\right]$

200 ml of 2-propanol were added drop by drop and with stirring to a filtered solution of 1.2g (1 mmole) of $(Nb_6Cl_{12})F_2\cdot 9H_2O$ in 100 ml of dimethyl sulfoxide. After two days the resulting, fine, dark green precipitate was filtered, washed with iso-propanol, then ether, and dried _in vacuo_ over phosphorus pentoxide.

Analysis: Found: Nb, 40.60%; Cl, 28.86%; Cl:Nb, 11.18:6.00. Calculated for $\left[(Nb_6Cl_{12})F_2\ (DMSO)_4\right]$ Nb, 41.81%; Cl, 31.91%.

Dimethyl formamide adduct of $(Nb_6Cl_{12})F_2$

Attempts were made to prepare a dimethyl formamide adduct of $(Nb_6Cl_{12})F_2$ in the same way as described above for the DMSO adduct. No uniform product was obtained.

$\left[(Nb_6Cl_{12})F_2\ (C_5H_5NO)_4\right]$

0.76g (8 mmoles) of dry, solid pyridine-N-oxide was added slowly and with stirring to a warm filtered solution containing 2.4g (2 mmoles) of $(Nb_6Cl_{12})F_2\cdot 9H_2O$ in absolute ethanol. After three days the fine dark green precipitate was filtered over a frit, washed with ethanol and ether and dried in vacuo over phosphorus pentoxide. Analysis: Found: Nb, 39.72%; Cl, 30.23%; Cl:Nb, 11.97:6.00. Calculated for $[(Nb_6Cl_{12})F_2\ (C_5H_5NO)_4]$: Nb, 39.78%; Cl, 30.36%.

$[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]\cdot 3CH_3CN$

1.2g (1 mmole) of $Nb_6Cl_{14}\cdot 4CH_3CN$ was dissolved in 50 ml of absolute ethanol. The filtered solution was saturated with dry HCl gas with constant stirring, and 0.25g (1 mmole) of iodine was added. After 5.0g of dry solid tetramethyl ammonium chloride had been added slowly with stirring, the reaction mixture was heated for 20 minutes to complete precipitation. 1.0g of the glittering black-brown product was collected on a fritted glass filter, washed with 1:2, 1:1, and 2:1 mixtures of absolute ethanol and chloroform, washed further with ether and dried in vacuo over phosphorus pentoxide. Analysis: Found: Nb, 36.85%; Cl, 42.17%; Cl:Nb, 17.99:6.00; N, 5.22%. Calculated for $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]\cdot 3CH_3CN$: Nb, 36.17%; Cl, 41.41%; N, 5.46%.

Reactions with thionyl chloride:

Reaction of $Nb_6Cl_{14}\cdot 8H_2O$ with thionyl chloride

20 ml of thionyl chloride were added with stirring to a filtered solution containing 1.2g (1 mmole) of $Nb_6Cl_{14}\cdot 8H_2O$ in 30 ml of absolute methanol. After the violent reaction had subsided, 10 or 20 ml portions of

thionyl chloride were added with stirring and moderate heating at 20 minute intervals until a total of 100 ml of thionyl chloride had been added. The reaction mixture was evaporated to 40 ml. After standing over night, the dark olive precipitate was filtered over a frit, washed with ether and dried _in vacuo_ over phosphorus pentoxide. Analysis: Found: Nb, 41.59%; Cl, 41.61%, Cl:Nb, 15.67:6.00.

A mull spectrum showed a peak at 4750 Å indicating $(Nb_6Cl_{12})^{4+}$-containing material.

Reaction of $Nb_6Cl_{14}\cdot 8H_2O$ with acetonitrile and thionyl chloride

50 ml of thionyl chloride was added drop by drop and with stirring to a filtered solution containing 2.4g (2 mmoles) of $Nb_6Cl_{14}\cdot 8H_2O$ in 25 ml of absolute methanol, to which 50 ml of acetonitrile had been added. After the violent reaction was completed, another 50 ml of thionyl chloride was added, and the mixture was refluxed for six hours. The olive precipitate was filtered, washed several times with ether, and again refluxed for four hours with 40 ml of acetonitrile and 40 additional ml of thionyl chloride. After cooling, the dark olive precipitate was filtered over a frit, washed with ether, then successively with 2:1, 1:1, and 1:2 mixtures of chloroform and absolute ethanol, again with ether, and finally dried _in vacuo_ over phosphorus pentoxide.

Analysis: Nb, 43.72%; Cl, 48.30%; Cl:Nb, 17.37:6.00.

Examination under a microscope revealed that the bulk of the product consisted of black microcrystalline material, mainly needles, and of a small amount of white crystalline material. A mull spectrum showed a peak at 4800 Å, indicating $(Nb_6Cl_{12})^{4+}$-containing material.

A second, light olive product, obtained by refluxing the reaction mixture only for 30 minutes, examined under the microscope was seen to contain mainly white crystalline material and few black needles.

A third product, obtained after the reaction mixture had been refluxed for 50 hours, consisted of dark microcrystalline material that contained no needles. A peak in the mull spectrum at 4800 Å indicated $(Nb_6Cl_{12})^{4+}$-containing material.

Analysis: Found: Nb, 24.23%; Cl, 43.46%; Cl:Nb, 28.09:6.00.

Analytical procedures

Niobium

Niobium was determined gravimetrically as the oxide, Nb_2O_5. Samples containing neither fluorine nor sulfur were weighed directly into a tared crucible, oxidized with concentrated nitric acid, dried and ignited.[14] Samples of fluorine- or sulfur-containing compounds were hydrolyzed in plastic beakers with aqueous ammonia. The hydrolysis products were carefully acidified with a few drops of concentrated nitric acid, and evaporated to dryness on a water bath. Water was added, and the white Nb_2O_5 hydrate was filtered onto medium retention filter paper, washed thoroughly with water, dried and ignited.

Halogens

Halogens were 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.[14]

Nitrogen

Nitrogen was sent to the Crobaugh Laboratories, Cleveland, Ohio, for analysis.

Physical measurements

X-ray diffraction

X-ray diffraction data were obtained with a 114.59 mm. Debye-Scherrer powder camera. Finely powdered samples were packed and hermetically sealed in 0.2 mm. Lindemann glass capillaries. These were exposed to Ni-filtered CuK_{α} radiation. Exposure time varied from 16 to 40 hours depending upon the sample.

Visible spectra

Visible spectra of solid materials were measured in the region 3800-5800 Å with a Cary Model 14 recording spectrophotometer equipped with a double-prism monochromator. The finely ground solid materials were mulled with Nujol and placed between thin glass plates.

CHAPTER IV

RESULTS AND DISCUSSIONS

Synthesis of $Nb_6Br_{14}\cdot 8H_2O$

All methods used for the preparation of $Nb_6Br_{14}\cdot 8H_2O$ involved a high-temperature synthesis of $(Nb_6Br_{12})^{2+}$-containing material. This material was extracted, and from the purified aqueous solution the hydrate was precipitated. The amounts of $Nb_6Br_{14}\cdot 8H_2O$ obtained via aluminum reduction of niobium pentabromide were rather disappointing. In comparison with the aluminum reduction the conproportionation of niobium pentabromide with niobium metal has several clear advantages. First, even at low yields it will supply rather large amounts of cluster material, since both oxidizing and reducing agent are transformed into the desired product. Second, since the reducing agent is niobium metal itself, an excess of it cannot overreduce the pentabromide to the metal. Third, this method does not use a molten salt as solvent, therefore, upon extraction with water, it does not introduce vast amounts of foreign substances into the aqueous solution.

The formation of $(Nb_6Br_{14})^{2+}$ cluster material in a high-temperature synthesis is facilitated if the cluster cation is stabilized by complexation into an $(Nb_6Br_{18})^{4-}$ anion. That was accomplished by addition of an alkali bromide according to the equation:

$$20ABr + 14NbBr_5 + 16\ Nb \longrightarrow 5A_4Nb_6Br_{18} \quad (4)$$

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

$$10ABr + 4NbBr_5 + Nb \longrightarrow 5A_4NbBr_6 \quad (5)$$

$$15ABr + 6NbBr_5 + 4Nb \longrightarrow 5A_3Nb_2Br_9 \quad (6)$$

$$ABr + 2NbBr_5 + 2Nb \longrightarrow ANb_4Br_{11} \quad (7)$$

which need alkali bromide/niobium pentabromide ratios of 5:2, 5:2, and 1:2, respectively. To favor the formation of $A_4Nb_6Br_{18}$, only the stoichiometric alkali bromide/niobium pentabromide ratio given by equation (4) was used.

Of great importance for the success of reaction(4) is the selection of the alkali bromide, ABr, since the relative stabilities of the compounds A_2NbBr_6, $A_3Nb_2Br_9$, and ANb_4Br_{11} competing with $A_4Nb_6Br_{18}$ are functions of the particular alkali ions, A^+. Of the species $A_3Nb_2Br_9$, only $Cr_3Nb_2Br_9$ and $Rb_3Nb_2Br_9$ have been synthesized so far;[28] and of the species ANb_4Br_{11}, only the cesium compound has been prepared.[29] For the composition A_2NbBr_6, it can be assumed that the stabilities follow a similar pattern as for the chlorides, where stabilities decrease from the cesium compound down to the sodium compound as pointed out by Parsons, Vongvusharintra, and Koknat.[30] For the type $A_4Nb_6Br_{18}$, however, only $K_4Nb_6Br_{18}$[15] and $Rb_4Nb_6Br_{18}$[13,15] have been reported, and the considerably higher yields indicate a greater stability for the potassium compound. Attempts by Broll, Juza, and Schäfer[15] to prepare $Cs_4Nb_6Br_{18}$ from Nb_3Br_8, niobium metal, and cesium bromide were unsuccessful. $Cs_3Nb_2Br_9$ and $CsNb_4Br_{11}$ were found to be formed instead. Since $K_4Nb_6Br_{18}$ is more stable than its heavier analogues and since, for the competing compounds, the heavier representatives seem to have greater stabilities, we selected KBr as complexing agent.

In addition to stabilizing the $(Nb_6Br_{12})^{2+}$ cation as an $(Nb_6Br_{18})^{4-}$ complex anion, the added alkali bromide serves another purpose. By complexing niobium pentabromide and niobium tetrabromide to non-volatile hexabromoniobates, it prevents the build-up of excessive pressure in the initial stages of the reduction. Since niobium metal and niobium subhalides react slowly with SiO_2 of the glass wall[15,31] to form Nb_5Si_3, an excess of the metal was used and the reaction was confined to a time of approximately one day. The lack of excessive pressure allowed a rapid initial heat-up and made it possible to react large quantities by "stuffing" the reaction tubes.

Temperature-time diagrams for several attempts involving reaction (4) are given, together with the obtained yields, in Figure 1. It can be seen that selection of the proper temperature is critical to the success of the reaction. The maximum yield of 81% was obtained at 720°C. Yields of 51% and 38% were obtained for reaction temperatures of 830°C and 620°C, respectively.

Several of the batches of $Nb_6Br_{14}\cdot 8H_2O$, prepared while attempting to find the best conditions for the forma-

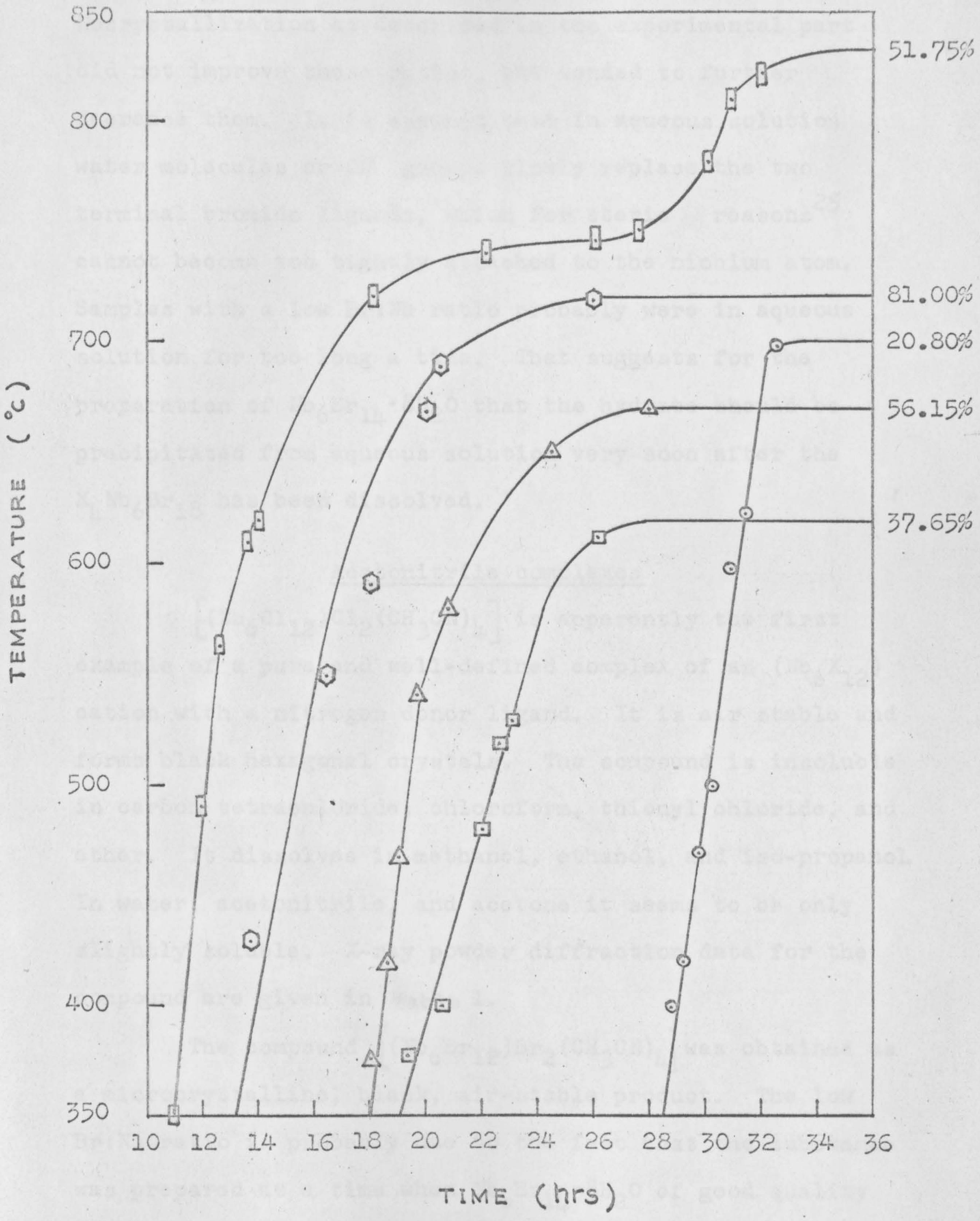

Fig. 1. Heating curves and yields for reaction (4)

tion of $K_4Nb_6Br_{18}$, showed Br:Nb ratios around 13.5:6. Recrystallization as described in the experimental part did not improve these ratios, but tended to further decrease them. It is assumed that in aqueous solution water molecules or OH^- groups slowly replace the two terminal bromide ligands, which for steric reasons[25] cannot become too tightly attached to the niobium atom. Samples with a low Br:Nb ratio probably were in aqueous solution for too long a time. That suggests for the preparation of $Nb_6Br_{14}\cdot 8H_2O$ that the hydrate should be precipitated from aqueous solution very soon after the $K_4Nb_6Br_{18}$ has been dissolved.

Acetonitrile complexes

$[(Nb_6Cl_{12})Cl_2(CH_3CN)_4]$ is apparently the first example of a pure and well-defined complex of an (Nb_6X_{12}) cation with a nitrogen donor ligand. It is air stable and forms black hexagonal crystals. The compound is insoluble in carbon tetrachloride, chloroform, thionyl chloride, and ether. It dissolves in methanol, ethanol, and iso-propanol. In water, acetonitrile, and acetone it seems to be only slightly soluble. X-ray powder diffraction data for the compound are given in Table 1.

The compound $[(Nb_6Br_{12})Br_2(CH_3CN)_4]$ was obtained as a microcrystalline, black, air-stable product. The low Br:Nb ratio is probably due to the fact that the substance was prepared at a time when $Nb_6Br_{14}\cdot 8H_2O$ of good quality

Table 1. X-ray diffraction data for $\left[(Nb_6Cl_{12})Cl_2(CH_3CN)_4\right]^a$

Relative[b] intensity	2θ, degrees	Observed "d" spacing Å
1	9.55	9.2607
9	10.38	8.5220
9	10.85	8.1539
1	11.50	7.6944
8	12.55	7.0529
1	20.35	4.3638
1	22.00	4.0401
1	23.66	3.7603
4	29.38	3.0399
1	32.48	2.7565
6	35.18	2.5509
1	36.63	2.4532
1	38.50	2.3382
1	40.73	2.2686
1	45.00	2.0144
1	46.70	1.9450
2	48.29	1.8846
3	52.70	1.7368
1	56.70	1.6234

[a] Exposure time for this pattern was 24 hours. Radiation used was Cu K_α.

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

was not yet available. The compound is insoluble in carbon tetrachloride and in acetonitrile. It can be dissolved in ethanol, in methanol, and in water. X-ray powder diffraction data are given in Table 2.

Adducts of $(Nb_6Cl_{12})F_2$

$(Nb_6Cl_{12})F_2 \cdot 9H_2O$, the starting material for the preparation of $(Nb_6Cl_{12})F_2$ adducts, has previously been prepared and described by Hughes, Meyer, Fleming, and McCarley.[20] Using their method a well-crystallized product of great purity was obtained.

The reaction of $(Nb_6Cl_{12})F_2 \cdot 9H_2O$ with pyridine-N-oxide yielded a pure product of the composition $\left[(Nb_6Cl_{12})F_2(C_5H_5NO)_4\right]$. Reactions with acetonitrile, dimethyl sulfoxide, and dimethyl formamide gave impure or non-uniform products. None of the products were investigated any further.

$\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6 \cdot 3CH_3CN\right]$

A compound corresponding to the formula $\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6\right] \cdot 3CH_3CN$ was obtained when attempting to use $Nb_6Cl_{14} \cdot 4CH_3CN$ as a starting material for the preparation of $\left[(CH_3)_4N\right]_2\left[(Nb_6Cl_{12})Cl_6\right]$. The $Nb_6Cl_{14} \cdot 4CH_3CN$ was dissolved in absolute ethanol, and the solution was saturated with dry hydrogen chloride gas. After sufficient iodine had been added to oxidize all $(Nb_6Cl_{12})^{2+}$ units to $(Nb_6Cl_{12})^{4+}$ units, a dark, glittering

Table 2. X-ray diffraction data for $\left[(Nb_6Br_{12})Br_2(CH_3CN)_4\right]^a$

Relative[b] intensity	2θ, degrees	Observed "d" spacing, Å
1	8.42	10.5010
10	9.41	9.3982
2	13.00	6.8098
2	13.63	6.4964
1	16.00	5.5391
1	18.78	4.7249
2	20.50	4.4394
2	21.40	4.1520
1	26.00	3.4269
9	28.50	3.1317
1	29.67	3.0109
4	30.68	2.9140
1	31.42	2.8470
3	32.30	2.7715
3	33.37	2.6850
3	34.72	2.5836
8	35.80	2.5081
4	37.26	2.4171
7	39.00	2.3094
1	40.50	2.2275
5	42.15	2.1438
2	43.00	2.1034
3	45.00	2.0144
1	47.00	1.9333
1	48.53	1.8758
6	51.00	1.7906
6	53.00	1.7277
1	55.65	1.6515
2	61.54	1.5068

[a] Exposure time for this pattern was 24 hours. Radiation used was Cu K_α.

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

product was precipitated by the addition of dry solid tetramethyl ammonium chloride.

Analyses showed that the product obtained has the desired theoretical Cl:Nb ratio of 18:6. Low chlorine and niobium values and a high nitrogen value indicated that the product could be neither $\left[(CH_3)_4N\right]_2\left[(Nb_6Cl_{12})Cl_6\right]$ nor $\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6\right]$. A mull spectrum showed a peak at 4450 Å indicating the presence of $(Nb_6Cl_{12})^{3+}$ units,[27] and an X-ray powder pattern (see Table 3) was found to be identical with a pattern of $\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6\right]$[32] (see Table 4).

These findings can be explained in the following way: $\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6\right]$ crystallizes in a lattice that contains a large amount of open space.[32] The $(Nb_6Cl_{18})^{3-}$ units are stacked in a cubic close packing, and 2/3 of the tetramethyl ammonium groups fill the tetrahedral holes in this lattice. The remaining tetramethyl ammonium groups are accommodated in the octahedral holes, which are approximately four times larger. The empty space left in each octahedral hole is more than sufficient to accommodate three acetonitrile molecules. Therefore, the product is formulated to be $\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6\right]\cdot 3CH_3CN$, which is in good agreement with the analytical data.

Reactions with thionyl chloride

Although the reactions with thionyl chloride did not yield uniform products, some conclusions can be drawn.

Table 3. X-ray diffraction data for $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]\cdot 3CH_3CN$[a]

Relative intensity[b]	2θ, degrees	Observed "d" spacing, Å
8	8.70	10.1630
10	9.30	9.5091
9	10.65	8.3065
6	14.67	6.0381
4	15.50	5.7166
6	18.00	4.9279
2	19.00	4.6707
2	22.35	3.9776
1	24.00	3.7078
1	24.47	3.6376
3	27.10	3.2903
2	31.50	2.8400
3	33.58	2.6687
7	36.05	2.4913
1	38.30	2.3500
6	39.00	2.3094
1	40.55	2.2246
2	41.65	2.1684
1	45.00	2.0144
1	45.65	1.9873
2	46.50	1.9529
1	48.78	1.8668
1	51.45	1.7760
1	54.00	1.6980
2	55.70	1.6502

[a] Exposure time for this pattern was 30 hours. Radiation used was CuKα.

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

Table 4. X-ray diffraction data for $\left[(CH_3)_4N\right]_3\left[(Nb_6Cl_{12})Cl_6\right]$[a]

Relative intensity[b]	2θ, degrees	Observed "d" spacing, Å
8	8.70	10.1630
10	9.30	9.5091
9	10.64	8.3043
6	14.67	6.0381
3	15.47	5.7276
6	18.00	4.9279
2	19.00	4.6707
1	22.30	3.9864
1	24.01	3.7063
4	28.25	3.1589
1	30.00	2.9785
1	31.00	2.8847
2	31.60	2.8312
1	32.50	2.7549
3	33.63	2.6648
7	36.10	2.4880
1	38.30	2.3500
5	39.00	2.3094
1	40.57	2.2236
3	41.55	2.1734
1	45.03	2.0132
1	45.60	1.9893
1	46.54	1.9513
1	49.00	1.8589
1	54.00	1.6980
2	55.83	1.6466

[a] Exposure time for this pattern was 30 hours. Radiation used was Cu Kα.

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

In addition to removing water, thionyl chloride acted as an oxidizing agent and produced $(Nb_6Cl_{12})^{4+}$ material. Thionyl chloride also caused the attachment of additional chloride ligands to the cluster cation.

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