

1963

Preparation and reactions of some lower tungsten halides and halide complexes

Theodore Martin Brown
Iowa State University

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Inorganic Chemistry Commons](#)

Recommended Citation

Brown, Theodore Martin, "Preparation and reactions of some lower tungsten halides and halide complexes " (1963). *Retrospective Theses and Dissertations*. 2522.
<https://lib.dr.iastate.edu/rtd/2522>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

This dissertation has been 64-3858
microfilmed exactly as received

BROWN, Theodore Martin, 1934-
PREPARATION AND REACTIONS OF SOME
LOWER TUNGSTEN HALIDES AND HALIDE
COMPLEXES.

Iowa State University of Science and Technology
Ph.D., 1963
Chemistry, inorganic

University Microfilms, Inc., Ann Arbor, Michigan

PREPARATION AND REACTIONS OF SOME LOWER
TUNGSTEN HALIDES AND HALIDE COMPLEXES

by

Theodore Martin Brown

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

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1963

TABLE OF CONTENTS

	Page
INTRODUCTION	1
PART I. PREPARATION AND REACTIONS OF SOME TUNGSTEN HALIDES	3
REVIEW OF PREVIOUS WORK	4
EXPERIMENTAL	12
RESULTS AND DISCUSSION	36
SUMMARY	67
SUGGESTIONS FOR FUTURE WORK	69
PART II. SPECTROPHOTOMETRIC AND SUSCEPTIBILITY STUDIES OF SOME TUNGSTEN(IV) COMPLEXES	72
REVIEW OF PREVIOUS WORK	73
EXPERIMENTAL	75
RESULTS AND DISCUSSION	82
SUMMARY	115
SUGGESTIONS FOR FUTURE WORK	116
BIBLIOGRAPHY	118
ACKNOWLEDGEMENTS	123

INTRODUCTION

Tungsten derives its name from the Swedish tungsten = heavy stone. Another common name, Wolfram (Wolfralm = Wolf's foam), resulted from the interference of the tungsten mineral in tin ores in the smelting of tin by slagging or eating up the tin. The metal was discovered by Scheele (1) in 1781. At present, the chief ores are wolframite (iron, manganese tungstate), scheelite (calcium tungstate), and stolzite (lead tungstate). The purification of tungsten from its ores is relatively simple. The wolframite is first converted to alkaline tungstate which is then changed into tungsten(VI) oxide. The oxide is reduced with hydrogen to give the pure metal. Among its more valuable commercial uses are the preparation of high-speed tool steels and incandescent-lamp filaments.

Due to their ease of preparation, the halides containing tungsten in its higher oxidation states such as plus five and plus six have received considerable attention. These compounds, especially tungsten hexachloride, have found commercial uses as catalysts in the polymerization of olefins (2), the alkylation of parafins with olefins to motor fuels (3), fluorocarbon manufacture (4), dehydrochlorination of polychloroethanes (5),

and organic synthesis (6).

On the other hand, only little interest has been shown in the lower halides of tungsten. This is apparently due to the difficulty with which these materials are obtained and their increased inertness as the oxidation state of tungsten in these compounds is decreased.

While the tungsten(IV) halides are unstable with regard to hydrolysis in the presence of moist air and undergo disproportionation on heating, the tetrahalodi(pyridine)tungsten(IV) compounds show exceptional stability in this respect. Thus the question arises as to whether these complexes retain the initial structure of the parent halide or have a unique structure of their own giving rise to this increased stability. To enlarge the chemistry of tungsten in its lower oxidation states, it seemed desirable to undertake a study of some of the lower halides of tungsten and their corresponding compounds. This dissertation is divided into two parts. Part I is concerned with the preparation and reactions of some tungsten halides while Part II is devoted to spectrophotometric and magnetic susceptibility studies of some tungsten(IV) complexes. Since this investigation was carried out on the chlorides and bromides of tungsten, only these halides will be discussed.

PART I. PREPARATION AND REACTIONS OF SOME TUNGSTEN HALIDES

REVIEW OF PREVIOUS WORK

The Preparation and Properties of Some Tungsten Halides

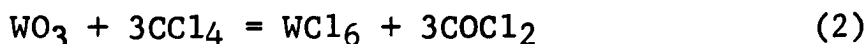
Tungsten(VI) halides

Direct chlorination of tungsten metal at temperatures greater than 600°C. results in the formation of the hexachloride as illustrated in Equation 1. If oxygen is present,



oxychlorides of tungsten are also formed. Oxygen and traces of moisture may be removed by first heating the metal in a stream of hydrogen at 700 to 1000°C. The resulting hexachloride is further purified by repeated sublimations (7, 8, 9, 10, 11).

Michael and Murphy (12) prepared tungsten(VI) chloride by heating carbon tetrachloride and tungsten(VI) oxide in a sealed tube. The reaction which takes place is illustrated in Equation 2. The necessary conditions to prevent the formation



of oxychlorides are: (1) excess carbon tetrachloride; (2) no oxygen or moisture present; and (3) sufficiently high temperature.

Other methods available for the preparation of tungsten(VI) chloride include the chlorination of tungsten(II) sulfide and

the action of phosphorus(V) chloride on tungsten(VI) oxide (13, 14, 15). However, in these cases the resulting product is difficult to purify.

Tungsten(VI) chloride is a dark violet or steel blue crystalline material, easily fused and volatilized. It has a melting point of 284°C . and a boiling point of 336.5°C . (16). The following transformations have been observed (16).

$$\text{solid } \alpha \text{ (} 152^{\circ} - 226.93^{\circ} \text{)} : \log p_{\text{mm}} = 10.732 - \frac{4582}{T} \quad (3)$$

$$\text{solid } \beta \text{ (} 226.93^{\circ} - 284^{\circ} \text{)} : \log p_{\text{mm}} = 9.255 - \frac{3837}{T} \quad (4)$$

$$\text{liquid (} 284^{\circ} - 362^{\circ} \text{)} : \log p_{\text{mm}} = 8.352 - \frac{3335}{T} \quad (5)$$

The heat of vaporization of the hexachloride has also been determined.

α vapor: 20.94 kcal/mole

β vapor: 17.54 kcal/mole

liquid vapor: 15.24 kcal/mole

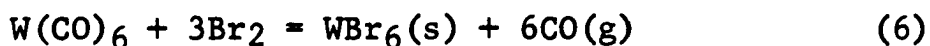
The electrical conductivity of liquid tungsten(VI) chloride was found to be very low and varied with temperature.

Electron diffraction shows that the WCl_6 molecule is a regular octahedron having a W-Cl distance of 2.26\AA (17). The same form has been observed in the solid by crystal structure measurements (18).

The hexachloride undergoes hydrolysis in the presence of

moist air but is relatively stable if very pure. In the presence of moisture the compound slowly transforms to the oxychloride, $WOCl_4$, and the hydrate, $WO_3 \cdot 2H_2O$.

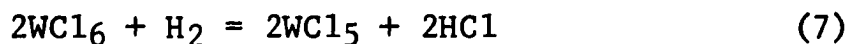
Tungsten(VI) bromide was first prepared by Schaffer and Smith (19) by passing a stream of nitrogen saturated with bromine vapor over warmed tungsten. The hexabromide sublimes readily and is deposited as blue-black needles. Due to the instability of this compound at elevated temperatures (it decomposes at temperatures greater than $200^\circ C$.) it is difficult to obtain free from lower bromides. More recently, Shchukarev, Novikov, and Kokovin (20) prepared this substance by reacting bromine with tungsten hexacarbonyl at $0^\circ C$. as illustrated by Equation 6.



In structure and properties tungsten(VI) bromide closely resembles the hexachloride.

Tungsten(V) halides

Reduction of tungsten(VI) chloride with hydrogen at $200^\circ C$., according to Equation 7, results in the formation of the penta-



chloride (7, 8, 21). The resulting product is separated from the other chlorides by sublimation in a stream of nitrogen.

This material is also one of the products resulting from the disproportionation of tungsten(IV) chloride. The pentachloride prepared by this method is relatively pure.

Tungsten(V) chloride is a deep purple-black solid which melts at 248°C . and boils at 276°C . Like the hexachloride, liquid tungsten(V) chloride has a relatively low electrical conductivity. The material is hygroscopic and sensitive to oxidation by the air. In this respect it is less stable than the hexachloride.

Direct combination of the elements at 800°C . results in tungsten(V) bromide (9, 21, 22). Generally some hexabromide is also formed if an excess of bromine is present. The pure pentabromide is obtained by subliming the product at temperatures greater than 200°C . with adequate provision for removing the bromine. Reduction of the hexachloride with hydrogen bromide at 250 to 300°C . yields the pentabromide (13).

The pentabromide is a crystalline brown-black solid melting at 286°C . and boiling at 392°C . with slight decomposition (20). The substance is unstable in air, undergoing hydrolysis and partially decomposing at elevated temperatures to give lower bromides. In the presence of oxygen, the oxybromide, WO_2Br_2 , is formed (13, 23). It is also possible to replace

the bromine to give chlorides, sulfides, and phosphides using hydrogen chloride, hydrogen sulfide, and phosphine, respectively.

Tungsten(IV) halides

The first synthesis of tungsten(IV) chloride involved the hydrogen reduction of tungsten hexachloride (7, 8, 21). Other methods of preparation include the chlorination of tungsten(IV) oxide with carbon tetrachloride in a sealed tube at 280°C. (12) and the reduction of tungsten(VI) chloride with red phosphorus (24).

Knecht and Hilbert (25) prepared tungsten(IV) chloride by the reduction of the hydrate, $WO_3 \cdot 2H_2O$, with zinc in concentrated hydrochloric acid. However, the anhydrous tetrachloride can not be isolated by this method.

The tetrachloride of tungsten is a crystalline, nonvolatile material which hydrolyzes readily. The compound disproportionates when heated above 300°C. to give the di- and pentachlorides of tungsten. The mechanism for this reaction is not known.

Tungsten(IV) bromide has been prepared by McCarley and Brown (26). The method used by these workers involved the reduction of tungsten(V) bromide with tungsten metal in a

sealed tube. A gradient furnace was used to heat the metal to 630°C . and the pentabromide in the opposite end of the tube to 340°C . However, this method gave rather low yields of the tetrabromide. Considering the similarities between the chlorides and bromides of tungsten(V) and (VI), one would expect that the tetrabromide could be prepared by methods similar to those used for the tetrachloride.

Tungsten(III) halides

Conspicuous for their absence among the known halides of tungsten are those of tungsten(III). Others (27) have attempted to prepare anhydrous tungsten trihalides, but were unsuccessful. Recently, McCarley and Brown (26) reported the preparation of tungsten(III) bromide from the reaction of tungsten(II) bromide with liquid bromine in a sealed tube at 55°C . From the information on tungsten halides, Brewer (28) estimated that the tungsten trihalides should not be thermally stable compounds. This was found to be the case for the tri-bromide which decomposed, when heated in vacuo at temperatures greater than 80°C ., to tungsten(II) bromide and bromine.

The only other tungsten(III) compounds known at the present time are confined to the anion complexes, e.g., $\text{W}_2\text{Cl}_9^{3-}$. The latter ion has been shown to have a dimeric

structure (29, 30) and is considered to be a derivative of the hypothetical dimer W_2Cl_6 . The complex anions of both the chloride (31) and the bromide (32) have been prepared.

Tungsten(II) halides

The methods available for preparing the dichloride of tungsten are: (1) hydrogen reduction of the hexachloride (7, 8, 21); (2) disproportionation of the tetrachloride of tungsten at $350^{\circ}C$. in a current of carbon dioxide; and (3) reduction of tungsten(VI) chloride with sodium amalgam (33) or aluminum (34).

The dichloride is a gray, nonvolatile solid. On heating to temperatures greater than $600^{\circ}C$. in the absence of air, the dichloride disproportionates into tungsten metal and higher tungsten chlorides.

The only method reported for preparing tungsten(II) bromide is the hydrogen reduction of the pentabromide at $400^{\circ}C$. (19, 21, 27). The dibromide is a green solid with properties very similar to those of tungsten(II) chloride.

The dihalides of tungsten are highly polymerized but their exact structure is not known. It is believed to be similar in structure to the molybdenum(II) halides which have a molecular formula Mo_6X_{12} .

Preparation and Properties of Tungsten(IV) Halide Complexes

There is a complete lack of information in the literature concerning the complexes of tungsten(IV) halides with organic ligands. Recently the preparation of pyridine adducts of niobium(IV) and tantalum(IV) were reported (35, 36). The niobium and tantalum tetrahalides were found to undergo reaction with pyridine readily to give di-pyridine adducts. It would be expected that tungsten(IV) halides should undergo similar reaction with pyridine and other organic ligands.

EXPERIMENTAL

Since some of the tungsten halides and their derivatives were susceptible to hydrolysis and oxidation by the air, sealed and evacuated glass vessels were used in all preparations and experiments. Storage and handling of these materials was done in a dry box under an argon atmosphere, which was maintained at a dew point of ca. -75°C . Sufficient drying of the argon was obtained by passing the gas over Linde 4A Molecular Sieves and maintaining an adequate supply of exposed magnesium perchlorate in the dry box.

Materials

Tungsten

Tungsten metal powder obtained from General Electric was used in all preparations. In experiments where oxygen could not be tolerated, tungsten was freed of oxygen by heating the metal in a stream of hydrogen at 1000°C . Analysis by emission spectroscopy showed the following elements to be present.

Oxygen.....	292 ppm	molybdenum.....	faint trace
hydrogen...	<10 ppm	chromium.....	faint trace
iron.....	faint trace		

Chlorine

Chlorine was obtained from the Mathison Company, Incorporated, in lecture size cylinders. The chlorine was distilled into the apparatus from the cylinder and outgassed on the vacuum line at -196°C . before beginning a reaction.

Bromine

Bromine, supplied by the J. T. Baker Chemical Company, was of reagent grade purity. The liquid was dried for two days under vacuum over well outgassed phosphorus(V) oxide. It was then vacuum distilled into a clean, evacuated flask for use in experiments as needed.

Organic reagents

The following organic compounds of high purity, were used in various experiments: pyridine, 4-ethyl pyridine, 4-picoline, 2,2'-bipyridine, benzene, carbon tetrachloride, and acetonitrile. All, except 2,2'-bipyridine, were thoroughly dried before use by placing them over well outgassed phosphorus(V) oxide. The reagent and drying material were then frozen, and the flask was completely outgassed. The liquids were vacuum distilled into clean, freshly outgassed flasks for storage. The 2,2'-bipyridine, which was solid at room temperature, was well outgassed before use without additional purification.

Analytical

The method of analysis varied with the type of compound being analyzed. Essentially these compounds fell into three categories: (1) volatile tungsten halides, (2) nonvolatile tungsten halides, and (3) complexes.

Volatile halides

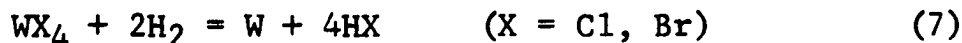
The tungsten(V) and (VI) halides were hydrolyzed in fifty per cent sodium hydroxide and boiled to assure complete hydrolysis. The solution was cooled and diluted to 250 ml. in a volumetric flask. Aliquots were taken for the tungsten and halide analyses.

For the tungsten analysis the solution was acidified with 6N nitric acid to a pH less than one and digested just below the boiling point for one hour. Five milliliters of a ten per cent cinchonine solution in 1:1 hydrochloric acid were then added, and the solution was digested for an additional hour. The tungsten(VI) oxide was then filtered, washed with 0.25 per cent cinchonine solution, ignited at 650°C. and weighed as the oxide, WO_3 .

Both chloride and bromide were determined by a Volhard titration after neutralizing the solution with 6N nitric acid.

Nonvolatile halides

Tungsten halides containing tungsten in an oxidation state of four and lower were very difficult to hydrolyze and oxidize to tungsten(VI) in sodium hydroxide. For these compounds a method involving hydrogen reduction was utilized. The apparatus for this procedure consisted of a straight vycor combustion tube with connections at each end for stopcocks. A known amount of sample in a small vycor vessel was placed in the combustion tube. A bubbler containing standard sodium hydroxide was attached to the outlet end of the combustion tube. Dry hydrogen was passed over the sample at a rate of one to two bubbles per second. A split furnace was placed around the combustion tube such that the sample was outside the furnace. The furnace, heated to 650°C., then was slowly moved toward the sample such that only a small portion of the sample reacted at any given time. During this period reduction occurred according to Equation 7. Hydrogen halide



produced during the reduction was passed through a known volume of standard sodium hydroxide. The total time required for the reduction was about five hours. The combustion tube was cooled to room temperature and taken into the drybox where

the sample vessel was removed. The tungsten was determined from the amount of tungsten metal obtained during the reduction. The hydrogen halide was determined by titrating the excess standard sodium hydroxide with standard hydrochloric acid.

Complexes

Due to the great stability of the tungsten complexes, it was not possible to analyze these compounds using the methods given above. For these materials it was necessary to determine the constituents on individual samples.

For the tungsten content, the sample was treated with concentrated nitric acid and digested until conversion to tungsten(VI) oxide was complete. This required about one hour. The tungsten was then determined gravimetrically using the procedure given for volatile halides.

The method of Jonassen, Cantor, and Tarsey (37) was used to determine the chloride content. In this procedure, a known amount of sample was heated in concentrated sulfuric acid for about three hours. The hydrogen chloride evolved during decomposition was transported in a stream of nitrogen to a ten per cent sodium hydroxide solution. A saturated aqueous solution of potassium dichromate then was added to the

sulfuric acid solution and heating was continued for several more hours to insure complete removal of the chloride. The chloride was determined by the usual Volhard titration.

In the case of samples containing bromide, the procedure was essentially the same as for the chloride except for the addition of sodium formate to the sodium hydroxide solution (38). Any bromine resulting from the oxidative nature of the sulfuric acid was reduced to bromide by this solution.

In the analysis of pyridine, samples were digested with concentrated sulfuric acid which resulted in complete solution of the samples along with the formation of pyridinium sulfate. The solutions were fumed almost to dryness. Concentrated sodium hydroxide was added and the pyridine was distilled into glacial acetic acid and titrated potentiometrically with perchloric acid in acetic acid (36).

Physical Measurements

X-ray diffraction

X-ray diffraction data were obtained with an 114.59 mm. Debye-Scherrer camera. Powdered samples, packed in 0.2 mm. Lindemann capillaries, were exposed to Ni-filtered $\text{CuK}\alpha$ radiation for periods of 16 to 20 hours. The conversion from θ values to interplanar distances was obtained from NBS

tables (39).

Magnetic susceptibility

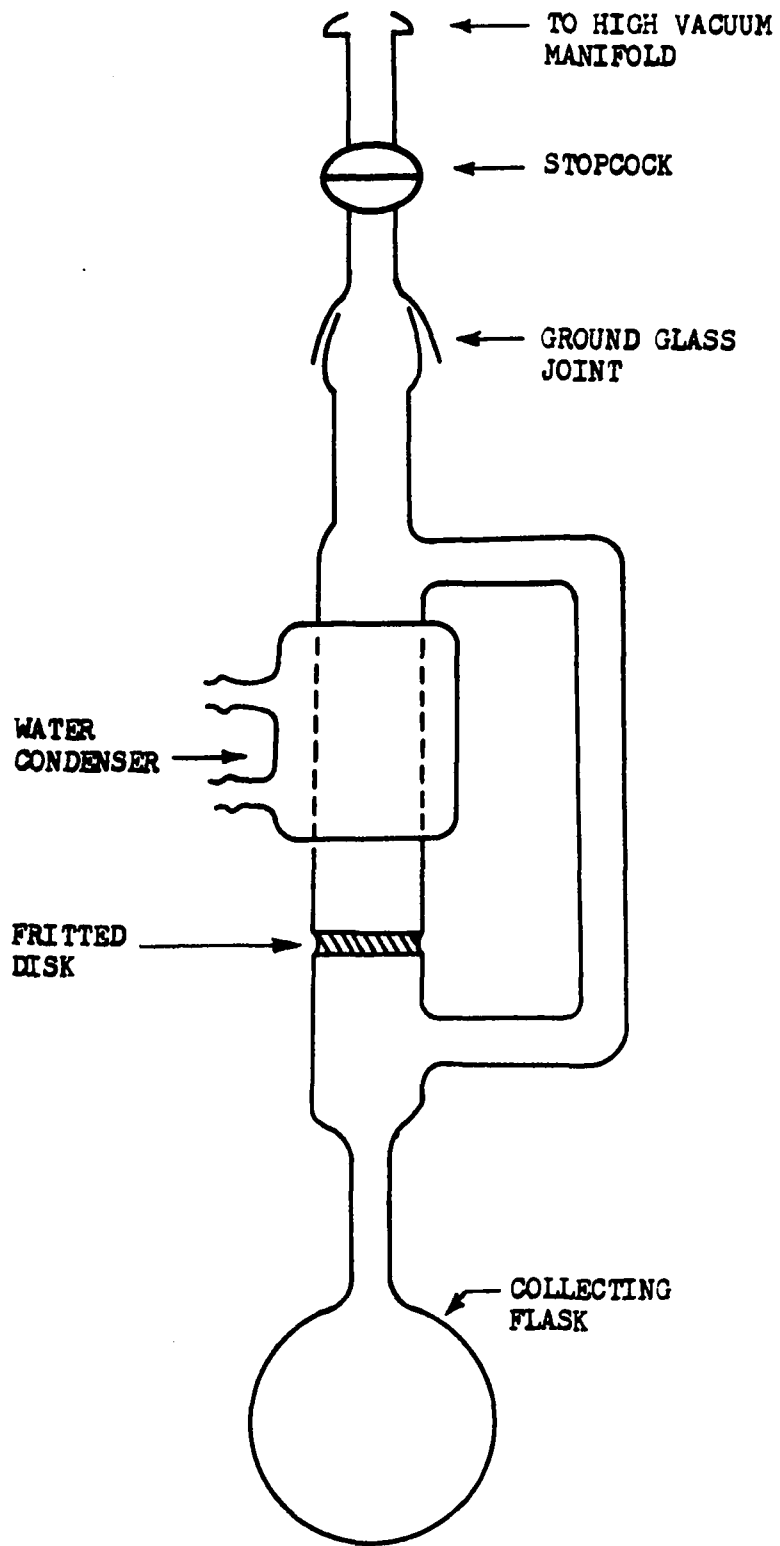
The magnetic susceptibility data were obtained by the Faraday method from -196°C . to room temperature by Mr. J. D. Greiner.

The samples were put through a 200-mesh sieve and placed in cylindrical Pyrex bulbs two centimeters long and one centimeter in diameter. These bulbs were connected to a stopcock by a narrow piece of Pyrex tubing ca. one millimeter in diameter. This small constriction allowed sealing off of the sample without decomposition. The bulbs were then outgassed on a vacuum line to ca. 10^{-5} Torr and sealed off before measurement. The weight of the sample was obtained by weighing the bulbs before and after filling with the sample. Corrections for diamagnetism of the Pyrex bulbs were made for all measurements.

Washing procedures

The metal halide-pyridine reaction mixtures were washed in an apparatus designed for continuous extraction (cf. Figure 1). The sample to be washed was placed in the extraction apparatus in a dry box. The apparatus was attached to a vacuum line and outgassed. Approximately 40-50 ml. of aceto-

Figure 1. Extraction apparatus



nitrile then was distilled into it. Continuous extraction was achieved by circulating cooling water through a condenser jacket at the top of the apparatus. The extraction was continued until the filtrate coming through the filter was colorless. The excess solvent then was distilled from the extractor, and the sample was removed from the apparatus in a dry box.

Oxidation-reduction titrations

The extent of the reduction in the reaction between tungsten(VI) chloride and tungsten(V) bromide and pyridine was determined using a method similar to that of Jonassen, Cantor, and Tarsey (37). A known excess of standard potassium dichromate was added to a weighed sample. The solution was acidified with several ml. of 6N sulfuric acid and heated near the boiling point for forty eight hours. During this time the tungsten was oxidized to tungsten(VI) oxide. The excess dichromate was determined by adding excess potassium iodide and titrating the resulting iodine with standard sodium thiosulfate using a starch indicator. In cases where bromide was also present, the evolved gases containing bromine were passed through an alkaline solution of potassium iodide. The solution then was acidified with 6N sulfuric acid and the resulting iodine titrated with standard sodium thiosulfate. The

equivalent weight of tungsten was then obtained from a combination of the excess dichromate and alkaline iodide titrations.

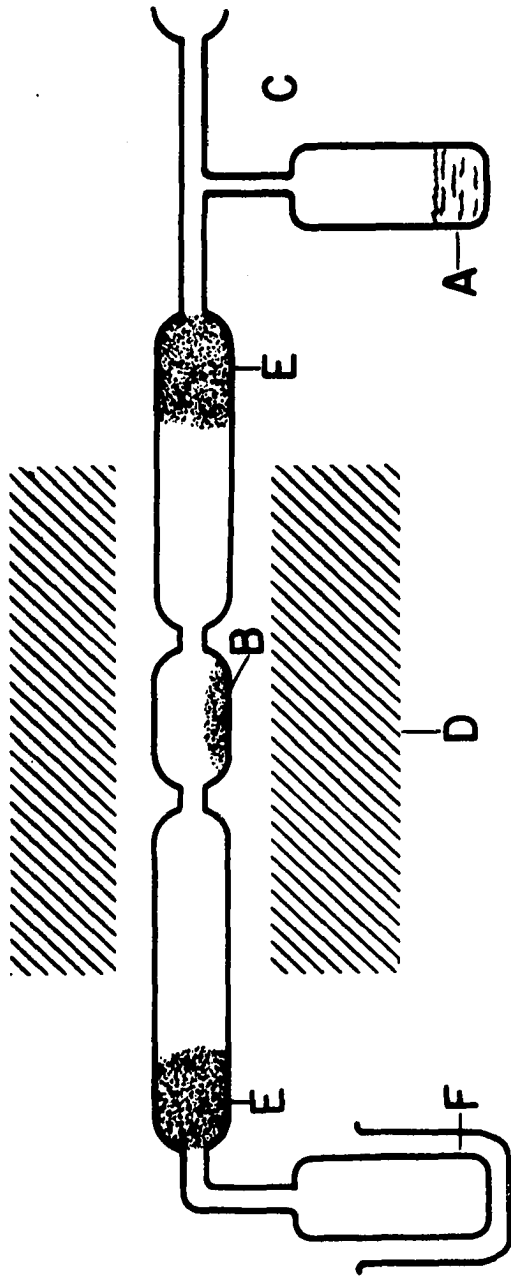
Synthesis

Tungsten(VI) chloride

The apparatus shown in Figure 2 was used to prepare tungsten(VI) chloride. About twenty-five grams of tungsten powder was placed in the middle bulb, B. The apparatus then was connected to the vacuum system and evacuated to ca. 10^{-5} Torr. A Dry Ice-acetone bath was placed around bulb A, and chlorine was distilled into the bulb until it was about three-quarters full. The chlorine was frozen with liquid nitrogen. The apparatus was outgassed to ca. 10^{-5} Torr and sealed off from the vacuum system at C. The chlorine was allowed to liquify, and the Dry Ice-acetone bath was replaced around bulb A.

A split furnace, D, was placed around the apparatus as shown, and the tungsten metal was heated to 600°C . Bulb F was placed in a Dry Ice-acetone bath, and the bath around A was removed. Chlorine readily distilled over the metal and the tungsten(VI) chloride sublimed into bulb E. The chlorine was redistilled back and forth over the metal until the chlorine was used up. Two to three days were necessary for

Figure 2. Apparatus used for the preparation of tungsten(VI) chloride and tungsten(V) bromide



the reaction to go to completion, i.e., to use up all the chlorine.

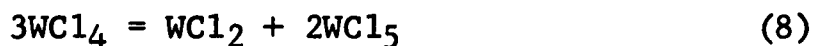
The furnace and reaction tube were cooled to room temperature and the tungsten(VI) chloride was transferred to sample bottles in the dry box until used in future experiments.

Anal. Calcd. for WCl_6 : W, 46.36; Cl, 53.64.

Found: W, 46.28; Cl, 53.59.

Tungsten(V) chloride

Tungsten(V) chloride was prepared by disproportionating tungsten(IV) chloride according to Equation 8.

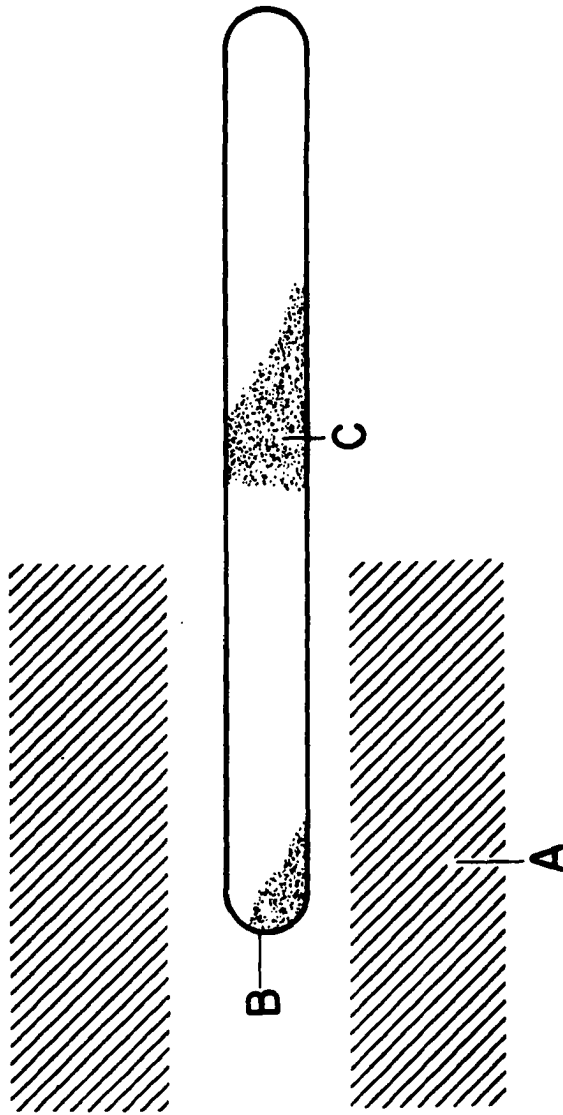


The reaction was performed in sealed evacuated tubes (cf. Figure 3). The end of the tube, B, containing tungsten(IV) chloride was heated to $450^{\circ}C$. while the opposite end was maintained at room temperature. As the reaction progressed the tungsten(V) chloride condensed near the cool end of the tube, C. The pentachloride was sublimed several times to insure complete removal of lower chlorides. The material was stored in the dry box in the same manner as was the hexachloride.

Anal. Calcd. for WCl_5 : W, 50.91; Cl, 49.09.

Found: W, 50.73; Cl, 48.95.

Figure 3. Apparatus used for the preparation of tungsten(II) and tungsten(V) halides



Tungsten(V) bromide

Tungsten(V) bromide was prepared in an apparatus (cf. Figure 2) similar to that used for tungsten(VI) chloride. The bromine was vacuum distilled into bulb A using an ice-water bath. The bromine was frozen in a Dry Ice-acetone bath and the system was outgassed and sealed off from the vacuum line. Bromine was distilled over the metal, which was heated to 750°C., by cooling bulb F in an ice-water bath and allowing the bromine in bulb A to warm to room temperature.

The above method resulted in a mixture of tungsten(VI) and tungsten(V) bromides having no definite composition. Analysis of one of the preparations gave the following results.

Anal. Calcd. for WBr₆: W, 27.72; Br, 72.28.

Calcd. for WBr₅: W, 31.51; Br, 68.49.

Found: W, 28.87; Br, 70.77 (hydrogen reduction)

Br/W = 5.65

Br, 70.63 (Volhard titration)

Pure tungsten(V) bromide was prepared by subliming the above mixture at 250 to 300°C. At this temperature the hexabromide decomposed as illustrated in Equation 9.



The mixture was placed in an L-shaped tube, outgassed and

sealed off from the vacuum system. The end containing the mixture was heated from 250 to 300°C. As the material sublimed to the cool end of the tube which was cooled in a Dry Ice-acetone bath, the tungsten(V) bromide was deposited outside the furnace while the evolved bromine solidified in the Dry Ice-acetone trap. The tungsten(V) bromide was stored in a manner similar to that for tungsten(V) and tungsten(VI) chloride.

Anal. Calcd. for WBr_5 : W, 31.51; Br, 68.49.

Found: W, 31.34; Br, 68.40.

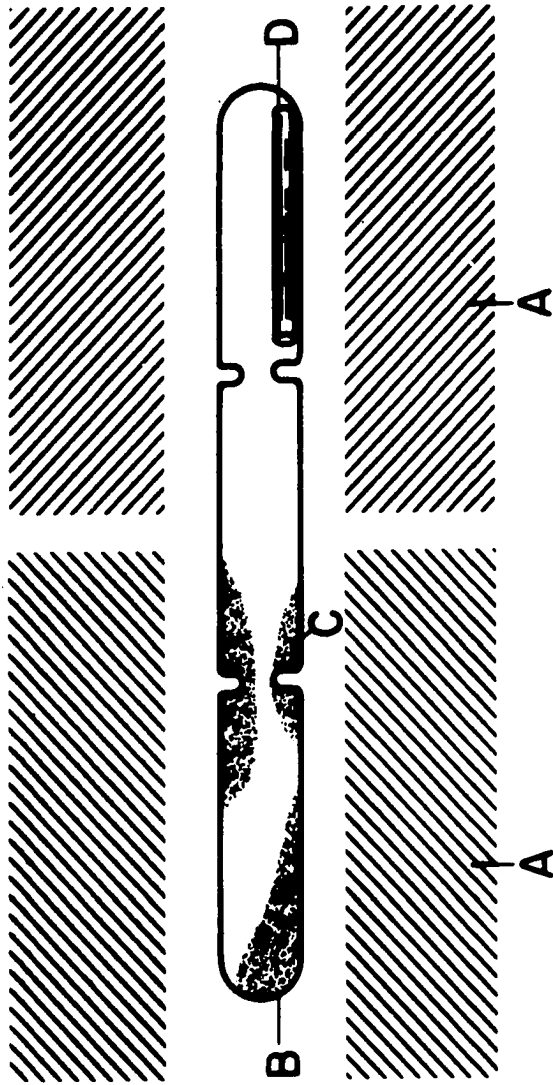
Tungsten(IV) chloride

Tungsten(IV) chloride was prepared in the apparatus shown in Figure 4. Aluminum foil, D, and a slight excess of tungsten(VI) chloride, B, needed for the reaction (cf. Equation 10) were placed in a straight Pyrex tube which was subsequently



evacuated and sealed. The reaction tube was placed in a double furnace so that one end (containing the aluminum) was maintained at 475°C., and the other end (containing the tungsten(VI) chloride) was maintained at 225°C. Approximately forty-eight hours was required for completion of the reaction. During the reaction, the tungsten(IV) chloride which formed

Figure 4. Apparatus used for the preparation of tungsten(IV) halides

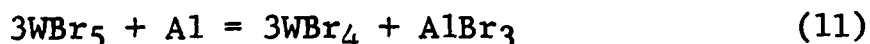


diffused to the cooler end of the tube and condensed as a coarse crystalline deposit. In order to free the product of excess tungsten(VI) chloride and aluminum chloride, which formed during the reaction, the end of the tube containing the crystalline deposit was heated to 325°C. while the opposite end was held at room temperature. The tube then was opened in the dry box, and the product was removed for analysis or subsequent experiments.

Tungsten(IV) bromide

Tungsten(IV) bromide was prepared by the same procedure as given for the preparation of tungsten(IV) chloride. In this case, however, the tungsten(V) bromide end was maintained at a temperature of 240°C. to give an appreciable vapor pressure of pentabromide. The aluminum end was maintained at 475°C.

Tungsten(V) bromide was used in slight excess of the amount needed for the reaction (cf. Equation 11). A black crystal-



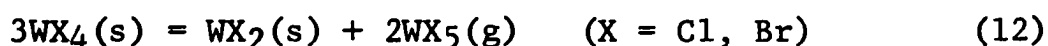
line material deposited near the cool end of the reaction tube. Excess pentabromide and aluminum bromide were removed by sublimation at 240°C.

Tungsten(IV) bromide was also prepared by reacting tungsten(V) bromide and tungsten metal according to the procedure

given above. In this case the tungsten metal was heated to 650°C. in a vycor tube while maintaining the other end of the tube at 240°C. The product was purified by the method outlined above. The product was removed in the dry box and stored until used in various reactions.

Tungsten(II) chloride and tungsten(II) bromide

Each of these compounds was prepared in a high state of purity by disproportionation of the appropriate tungsten(IV) halide as illustrated by Equation 12. The reactions were per-



formed in sealed Pyrex tubes according to the procedure outlined for the preparation of tungsten(V) chloride. The dihalide was placed in a straight vycor tube, and the sample was heated for a few minutes at 600°C. to remove any additional impurities. Although these materials appeared to be stable in the presence of air, they were stored in the dry box.

Reaction of tungsten(II) halides with liquid bromine

The reactions between tungsten(II) halides and liquid bromine were carried out in L-shaped tubes to which a ball joint was connected. The sample was placed in one end of the tube, attached to a vacuum line, and outgassed. Bromine was distilled into the vessel by cooling the end containing the

sample in an ice-water bath. The bromine was frozen in Dry Ice-acetone, and the apparatus was outgassed and sealed off from the vacuum system. After the bromine had melted, the vessel was shaken for two weeks in a water bath maintained at 55°C. The vessel was removed, and the bromine was distilled to the opposite end of the tube, frozen and sealed off from the product. The products were stored in the dry box.

Reaction of tungsten(V) and tungsten(VI) halides with pyridine

In order to check the possible reduction of tungsten(VI) chloride and tungsten(V) bromide with pyridine, as reported previously for the reduction of niobium(V) halides with pyridine, reactions between liquid pyridine and the tungsten halides were carried out. Known amounts of the appropriate halide were transferred to separate flasks equipped with a stopcock and ball joint for attachment to the vacuum manifold. The flask and contents were evacuated and weighed, and 60 to 70 ml. of pyridine were subsequently distilled into the vessel. After approximately one week of stirring at room temperature excess pyridine was removed by distillation and the product dried on a vacuum line. The flask and product were weighed. The crude products were washed with acetonitrile which removed all reaction products except the pyridine complex. The

products were stored in the dry box.

Reaction between tungsten(VI) and tungsten(V) chloride and pyridine

Reactions were also carried out between tungsten(V) and tungsten(VI) chloride and pyridine in carbon tetrachloride as a solvent by the procedure outlined above. In this case only a slight excess of pyridine over the stoichiometric amount necessary for the assumed reaction was used.

Reaction between tungsten(IV) halides and various organic ligands

Reactions were also carried out between tungsten(IV) halides and pyridine, 4-picoline, and 4-ethylpyridine. The reactions were carried out in flasks similar to those used for the reaction between tungsten(VI) halides and pyridine. Approximately one week was allowed for the reactions to go to completion. The solvents were removed by distillation, and the products were dried on the vacuum line. The products were stored in sample bottles in the dry box.

Reaction between tungsten(IV) halides and 2,2'-bipyridine

A known amount of the tungsten(IV) halide was placed in a flask. Excess solid 2,2'-bipyridine was added to the halide, and the flask was outgassed on the vacuum line. The flask and

its contents were heated in an oil bath to 100°C. for three days. The excess 2,2'-bipyridine was removed by sublimation at 100°C. The product was removed from the flask and stored in the dry box for future use.

RESULTS AND DISCUSSION

Preparation of Halides

Tungsten(V) and tungsten(VI) halides

The methods used for preparing these halides as outlined in the experimental section gave the most satisfactory yields of pure tungsten(VI) chloride and tungsten(V) bromide. Other methods were examined in the laboratory such as using an inert gas stream to carry the halogen over the metal. However these methods added impurities to the sample and caused a considerable waste of halogen. By distilling the halogen back and forth over the metal in a sealed vessel these disadvantages were avoided.

Tungsten(IV) halides

The principle methods reported for the preparation of tungsten(IV) chloride include: (1) reduction of tungsten(VI) chloride with hydrogen (7, 8, 21); (2) chlorination of tungsten(IV) oxide with carbon tetrachloride in a sealed tube (12); and (3) reduction of the hexachloride with red phosphorus (24). Because each of these methods suffers at least one serious disadvantage (e.g. high pressure reaction for (1) and (2), and difficulty in purification of product for (1) and (3)) a more convenient method for the synthesis of the

compound was sought.

Although a method for the preparation of tungsten(IV) bromide by reduction of the pentabromide with tungsten metal had been reported by McCarley and Brown (26), the reaction gave low yields and was very slow. Schäfer and Grau (40) reported the synthesis of lower tantalum halides by reduction of tantalum(V) halides with aluminum. Substitution of aluminum for the tungsten resulted in a much more rapid reaction and gave very good yields. This method was applied to the preparation of tungsten(IV) chloride with equal success. The compounds were analyzed using the hydrogen reduction method as outlined in the experimental section.

Anal. Calcd. for WCl_4 : W, 56.45; Cl, 43.55.

Found: W, 56.45; Cl, 43.10; Cl/W, 3.96.

Calcd. for WBr_4 : W, 36.52; Br, 63.48.

Found: W, 36.63; Br, 63.45; Br/W, 3.99 (Sample prepared by the reduction of tungsten(V) bromide with tungsten metal.)

Found: W, 36.21; Br, 62.77; Br/W, 3.99 (Sample prepared by the reduction of tungsten(V) bromide with aluminum metal.)

It was necessary to maintain the temperature of the higher

halide such that there was sufficient vapor pressure of the halide over the aluminum. This resulted in an increased rate of reaction. Too high a temperature increased the vapor pressure of the aluminum halide sufficiently to cause explosions. It was equally important to maintain a slight excess of the higher halide to prevent disproportionation of the tetrahalide. It was found that by using the conditions given in the experimental section, a one hundred per cent yield of tetrachloride and sixty to eighty per cent yield of tetrabromide was obtained over a two to three day period.

The tetrahalides of tungsten were black in both the crystalline and powder forms. In the presence of moist air they underwent hydrolysis to hydrogen halide and a mixture of oxyhalides and hydrated tungsten(VI) oxide.

X-ray diffraction data of these compounds were obtained using the method outlined in the experimental section. The d-spacings were compared with the d-spacings for niobium(IV) halides (35) and tantalum(IV) halides (36). This comparison showed that the tetrahalides of tungsten were isomorphous with those of niobium and tantalum. A comparison of the lattice constants for these compounds, given in Table 1, further verified that this was the case.

Table 1. Lattice constants of MX_4 compounds (M = Nb, Ta, and W)

Compound	a, Å	b, Å	c, Å
NbCl ₄	8.12	8.88	6.84
TaCl ₄	8.16	8.92	6.80
WCl ₄	8.07	8.89	6.85
NbBr ₄	8.60	9.31	7.19
TaBr ₄	8.58	9.30	7.21
WBr ₄	8.49	9.29	7.25

X-ray diffraction powder patterns of the solids were indexed on an orthorhombic unit cell of dimensions: $a = 8.07$, $b = 8.89$, $c = 6.85\text{Å}$ and $a = 8.49$, $b = 9.29$, $c = 7.25\text{Å}$ for WCl₄ and WBr₄ respectively. A comparison of the observed and calculated d-spacings for tungsten(IV) chloride and tungsten(IV) bromide is shown in Tables 2 and 3, respectively.

The calculated d-spacings given above were obtained using the following relationship for a solid which belongs to the orthorhombic crystal system:

$$1/d^2 = (h/a)^2 + (k/b)^2 + (l/c)^2. \quad (13)$$

The comparison is quite good. However, if the space group were known the forbidden planes of reflection could be determined, and additional refinement of the lattice constants

Table 2. X-ray diffraction data for tungsten(IV) chloride

$d_{\text{obsd.}}^a$ Å	$d_{\text{calcd.}}$ Å	hkl	$d_{\text{obsd.}}^a$ Å	$d_{\text{calcd.}}$ Å	hkl
5.97 (VVS)	5.97	110	1.93 (VVW)	1.94	401
4.45 (VVS)	4.45	020		1.94	213
4.02 (VVS)	4.03	200	1.86 (VVW)	1.86	042
3.23 (VS)	3.20	012		1.87	241
	3.24	211	1.84 (VVW)	1.84	420
3.03 (VVW)	2.99	220	1.81 (VVW)	1.81	033
	2.97	112		1.82	142
2.85 (VW)	-----	---		1.81	223
2.77 (W)	2.78	130	1.76 (VVW)	1.77	133
	2.74	221	1.73 (VVW)	1.73	150
2.62 (VS)	2.61	202		1.74	402
2.58 (S)	2.58	310		1.74	303
	2.57	122	1.71 (VW)	1.71	004
	2.58	131		1.72	051
2.54 (W)	2.51	301		1.71	412
2.23 (S)	2.22	040		1.72	332
	2.21	013		1.71	341
	2.24	032		1.71	313
	2.25	222	1.68 (VVW)	1.68	104
2.18 (VVW)	2.20	103		1.68	014
	2.18	321		1.68	151
2.13 (VW)	2.14	140	1.61 (VW)	1.61	500
	2.13	113		1.61	422
2.10 (W)	2.11	041	1.59 (VW)	1.58	510
	2.12	302		1.59	043
2.02 (S)	2.02	400		1.58	251
	2.03	023			
2.00 (W)	1.99	203			
	1.99	330			
1.98 (VVW)	1.97	410			
	1.97	123			

^aRelative intensity values are given in parenthesis. The terms used for intensity are: V = very, W = weak, and S = strong.

Table 3. X-ray diffraction data for tungsten(IV) bromide

$d_{\text{obsd.}}^a$ Å	$d_{\text{calcd.}}$ Å	hkl	$d_{\text{obsd.}}^a$ Å	$d_{\text{calcd.}}$ Å	hkl
6.45 (VVS)			1.85 (VW)	1.84	303
ave. 6.32	6.27	110		1.86	050
6.20 (VVS)				1.86	133
4.69 (VS)	4.65	020	1.81 (VS)	1.81	004
4.24 (VS)	4.24	200		1.80	313
3.42 (VW)	3.41	211		1.81	150
3.08 (W)	3.09	030		1.81	332
2.99 (VW)	3.14	112		1.80	313
	3.13	220	1.76 (VW)	1.77	104
2.89 (VW)	2.91	130		1.78	014
	2.88	221		1.75	430
2.75 (VVS)	2.76	202		1.76	151
2.68 (S)	2.70	131		1.77	242
2.35 (VS)	2.35	032	1.71 (VW)	1.70	500
	2.34	013		1.70	150
	2.37	222		1.71	422
2.29 (VW)	2.29	321		1.70	431
2.25 (VW)	2.24	140	1.66 (W)	1.67	043
	2.27	132		1.65	052
	2.25	113		1.66	501
2.21 (W)	2.21	041		1.67	510
2.13 (S)	2.13	400		1.66	124
	2.14	023	1.59 (W)	1.59	403
2.05 (VW)	2.07	410		1.59	520
	2.05	213		1.58	333
	2.04	401	1.56 (VW)	1.56	034
	2.04	240		1.57	224
	2.06	232		1.57	413
1.99 (VW)	2.01	322		1.56	440
	2.01	331		1.56	521
1.97 (VW)	1.96	042	1.54 (W)	1.53	304
	1.96	204		1.55	350
1.93 (VW)	1.93	420		1.54	502
1.90 (VW)	1.90	223		1.55	060
	1.90	142		1.53	441

^aRelative intensity values are given in parenthesis. The terms used for intensity are: V = very, W = weak, and S = strong.

could be made. To date no good single crystals have been prepared which are necessary for this determination. The best method for obtaining single crystals appeared to be the preparation of tungsten(IV) chloride from tungsten(II) chloride and tungsten(V) chloride. Several crystals of the tetrachloride have been obtained by heating the dichloride in the presence of the pentachloride. This preparation was carried out in a gradient furnace with the dichloride end maintained at a temperature of 400°C. and the pentachloride end at 300°C. The tetrachloride sublimed to an intermediate temperature zone in the tube where it deposited as needle-like crystals which were stable in the presence of excess pentachloride.

Magnetic susceptibility data of the tetrahalides of tungsten showed them to be diamagnetic. The diamagnetism was -58×10^{-6} e.m.u./mole and -75×10^{-6} e.m.u./mole at room temperature for the tetrachloride and tetrabromide, respectively. As there are two unpaired electrons present, paramagnetism would be expected if no direct metal-metal bonding occurred. If the diamagnetism of the tungsten(IV) halides is a result of direct metal-metal bonding, one might predict a chain structure as is observed in niobium(IV) iodide (41). The work on the tetraiodide gives a structure consisting of

infinite chains of NbI_6 octahedra sharing two opposite edges. Due to the metal-metal interaction, the niobium atoms are displaced from the centers of the octahedra in pairs. While the tungsten(IV) halides can be shown to be isomorphous with the chlorides and bromides of niobium, these tetrahalides are not isomorphous with the iodide of niobium. It is reasonable, however, to suspect a modification of the niobium(IV) iodide structure as one probable structure for the tungsten(IV) halides.

Tungsten(II) halides

Several methods were tried to prepare pure tungsten(II) chloride. The first method involved the reduction of the hexachloride with hydrogen at high pressure. Tungsten(IV) chloride was reduced with hydrogen in an autoclave using a hydrogen pressure of 250 psi and a reaction temperature of 190°C . Although reduction was obtained, the product contained not only the dichloride of tungsten but also higher chlorides.

The reduction of the hexachloride with aluminum powder was also attempted. Tungsten(VI) chloride was mixed with powdered aluminum in a sealed tube. A violent reaction took place at 75°C . resulting in a mixture of the dichloride and higher chlorides. Apparently the aluminum was too fine and

a coarser grade of aluminum would have given better results.

In another method, the reduction of the hexachloride was carried out with zinc in molten zinc chloride. Although reduction occurred, the zinc and zinc chloride were difficult to remove from the resulting product.

Tungsten(II) chloride and tungsten(II) bromide were prepared in a high state of purity by disproportionation of the appropriate tungsten(IV) halide in vacuo. The compounds were analyzed using the hydrogen reduction method as outlined in the experimental section.

Anal. Calcd. for WCl_2 : W, 72.17; Cl, 27.83.

Found: W, 72.11; Cl, 27.67; Cl/W, 1.99.

Calcd. for WBr_2 : W, 53.50; Br, 46.50.

Found: W, 53.22; Br, 46.43; Br/W, 2.01.

The dichloride was obtained free of higher chlorides at $450^\circ C$. It was necessary to heat the dibromide to $600^\circ C$. for a short period of time to remove the last traces of higher bromides. The advantage of this method is that the higher halide can be obtained pure and used in other reactions.

The higher halide formed during the disproportionation is the tungsten(V) halide. The pentabromide would be the expected product of the disproportionation of tungsten(IV)

bromide as the hexabromide is unstable and would decompose under the conditions used in this preparation of the dihalide. The disproportionation of the tetrachloride on the other hand could yield either the penta- or hexachloride. Analysis of the product definitely shows that tungsten(V) chloride is the resulting product (see p. 25).

The d-spacings observed for the dihalides are given in Table 4. From the data in Table 4, it appears that these two compounds are isomorphous.

Table 4. X-ray diffraction data for tungsten(II) chloride and tungsten(II) bromide

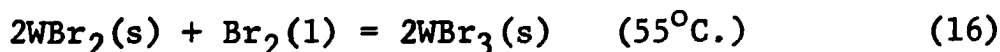
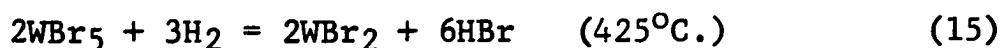
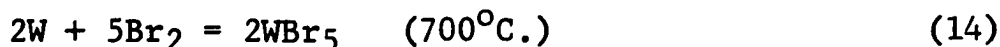
WCl ₂		WBr ₂	
d _{obsd.} ^a Å	d _{obsd.} ^a Å	d _{obsd.} ^a Å	d _{obsd.} ^a Å
6.94(10)	2.05(3)	7.31(10)	2.15(6)
5.63(9)	2.00(1)	5.91(5)	2.09(3)
3.47(3)	1.92(1)	3.63(2)	2.05(3)
2.88(5)	1.93(2)	2.72(5)	2.02(3)
2.61(5)	1.75(1)	2.64(4)	2.00(3)
2.52(1)	1.47(3)	2.48(2)	1.89(1)
2.37(1)		2.46(2)	1.86(4)
2.32(1)		2.42(2)	1.85(2)
2.20(5)		2.30(6)	1.82(4)
2.09(1)		2.18(2)	1.54(5)

^aRelative intensity values are given in parenthesis. All intensities were estimated relative to a value of 10 for the most intense line.

The magnetic susceptibility of the tungsten(II) halides was determined by Klemm and Steinberg (42). The compounds were found to be diamagnetic. The diamagnetism of these compounds and the complex powder patterns suggest a polymeric structure. The structure of the aqueous ions of $\text{Mo}_6\text{X}_8^{+4}$ has been determined (30, 43, 44, 45). It was shown to consist of a cube with eight halide atoms at the corners and a molybdenum atom in each of the six faces. In the solid dihalide one might expect a similar structure with the four additional halide atoms attached to four of the faces of the cube. The great resemblance between the complexes of molybdenum(II) and tungsten(II) makes it fairly certain that the tungsten(II) halides have the same sixfold structure as those of molybdenum and are W_6X_{12} .

Tungsten(III) halides

A compound having the composition corresponding to WBr_3 was prepared from tungsten and bromine. The following reactions were utilized for its preparation.



In the initial attempts to prepare the tungsten(III)

bromide, the dibromide was placed on a fritted disk in an extraction vessel. The material was extracted with liquid bromine at 30°C. for several days. Upon evaporation of the excess bromine, a black residue remained in the vessel below the frit indicating the formation of a soluble compound between tungsten(II) bromide and bromine.

Due to the extremely low yields, direct contact between the dibromide and liquid bromine was made in a sealed vessel at 55°C. The resulting material was extracted with liquid bromine, but only a small amount was extracted indicating a low solubility in bromine. A study of the black powder remaining after two weeks contact between tungsten(II) bromide and liquid bromine indicated the formation of a new compound. An x-ray diffraction powder pattern of the resulting compound did not indicate the presence of any of the known bromides. Chemical analyses on several samples of the product indicated the formula WBr_3 .

Anal. Calcd. for WBr_3 : W, 43.40; Br, 56.60.

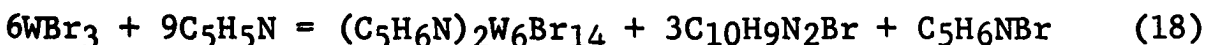
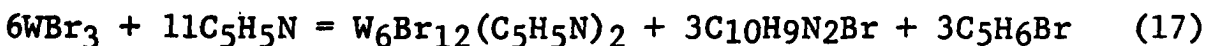
Found: W, 43.22 ± 0.07 ; Br, 56.30 ± 0.56 .

An equivalent weight determination made on the compound gave a value of 62.9 equivalents/mole which is in close agreement with the theoretically expected value of 61.3 equivalents/

mole for a tungsten(III) compound.

Additional information indicating a compound with tungsten having a plus three formal oxidation state was the reaction between the tribromide and liquid pyridine. A sample was stirred magnetically with excess liquid pyridine for approximately one week. After this time, the excess pyridine was removed. A green material remained behind. Weight gain data obtained after the reaction indicated a pyridine/WBr₃ mole ratio which varied between 1.5 and 1.7. Thus it was apparent that either the pyridine had formed a complex with tungsten(III) bromide or caused reduction to take place. The resulting product was analyzed for tungsten and an equivalent weight determination was carried out. An equivalent weight of 44.4 equivalents/mole was obtained for the tungsten present which agrees fairly well for the theoretical value of 46.0 equivalents/mole for a tungsten(II) compound. The presence of 1-(4-pyridyl)pyridinium ion in the reaction mixture was identified from its characteristic behavior and UV spectrum in aqueous sodium hydroxide solution (46). X-ray diffraction patterns also indicated the presence of pyridinium bromide (cf. Table 5). Attempts to extract the oxidation products with acetonitrile were not very successful

due to the solubility of the tungsten-pyridine complex in acetonitrile. Possible modes of reduction occurring between tungsten(III) bromide and pyridine are illustrated in Equations 17 and 18.



$\text{C}_{10}\text{H}_9\text{N}_2^+$ is the 1-(4-pyridyl)pyridinium ion; $\text{C}_5\text{H}_6\text{N}^+$ is the pyridinium ion. The pyridine/WBr₃ mole ratio for Equation 17 is 1.83 and for Equation 18 is 1.50. These values are within the range of those observed experimentally.

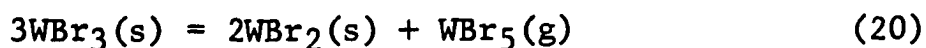
Table 5. X-ray diffraction data for the product obtained from the reaction between tungsten(III) bromide and pyridine

$d_{\text{obsd.}}^a$	$d_{\text{obsd.}}^a$	$d_{\text{obsd.}}^a$	$d_{\text{obsd.}}^a$
12.00 (VVS)	4.30 (W)	2.88 (W)	2.25 (VW)*
11.47 (VVS)	4.17 (W)	2.78 (W)	2.18 (VW)
8.86 (VVS)	4.07 (VW)	2.70 (W)	2.06 (W)
7.85 (W)	3.98 (W)*	2.61 (VW)	2.01 (VW)*
7.26 (S)*	3.60 (W)*	2.48 (VW)*	1.97 (VW)
6.77 (W)	3.55 (W)	2.44 (W)	1.95 (W)
6.28 (VS)	3.42 (VW)	2.41 (W)	1.83 (VW)
5.92 (W)	3.35 (VW)	2.37 (VW)	1.67 (VW)*
5.34 (S)*	3.29 (W)	2.31 (W)	1.58 (VW)*
4.43 (W)	3.06 (VW)	2.27 (W)	

^aRelative intensity values are given in parenthesis. The terms used for intensity are: V = very, W = weak, S = strong.

*Denotes lines also appearing on the x-ray diffraction powder pattern of pyridinium bromide.

An examination of the effect of heat on the tribromide showed this compound to be thermally unstable. At about 80°C. in vacuo decomposition into tungsten(II) bromide and bromine became noticeable. The decomposition at this temperature was very slow, but accelerated with increasing temperature. At 300°C. the decomposition was rapid and complete; only at the latter temperature was a relatively small amount of a volatile higher bromide formed. X-ray diffraction powder patterns of this volatile fraction showed that the major constituent was tungsten(V) bromide. The presence of the pentabromide as one of the decomposition products may be explained as a reaction between tungsten(II) bromide and bromine or a disproportionation of the trihalide at the elevated temperature as shown in Equations 19 and 20.



Tungsten tribromide is relatively stable in water, concentrated hydrochloric acid and air. The compound closely resembles molybdenum tribromide in this respect. Attempts to prepare chloride or bromide complexes from tungsten tribromide and aqueous hydrohalic acids were unsuccessful because of the low solubility of the solid. This apparent low solubility in

water and relative stability in air suggest that the solid tribromide exists in a polymerized form rather than a simple structure. The solid is slightly soluble in some polar solvents, e.g. nitroethane, nitrobenzene, and acetonitrile, producing wine-red solutions.

The magnetic susceptibility measurements obtained for this compound were somewhat unusual. The values obtained for χ_M as a function of temperature are given in Table 6 and plotted in Figure 5. The data suggest antiferromagnetism in the material with a Neel point occurring at higher temperatures.

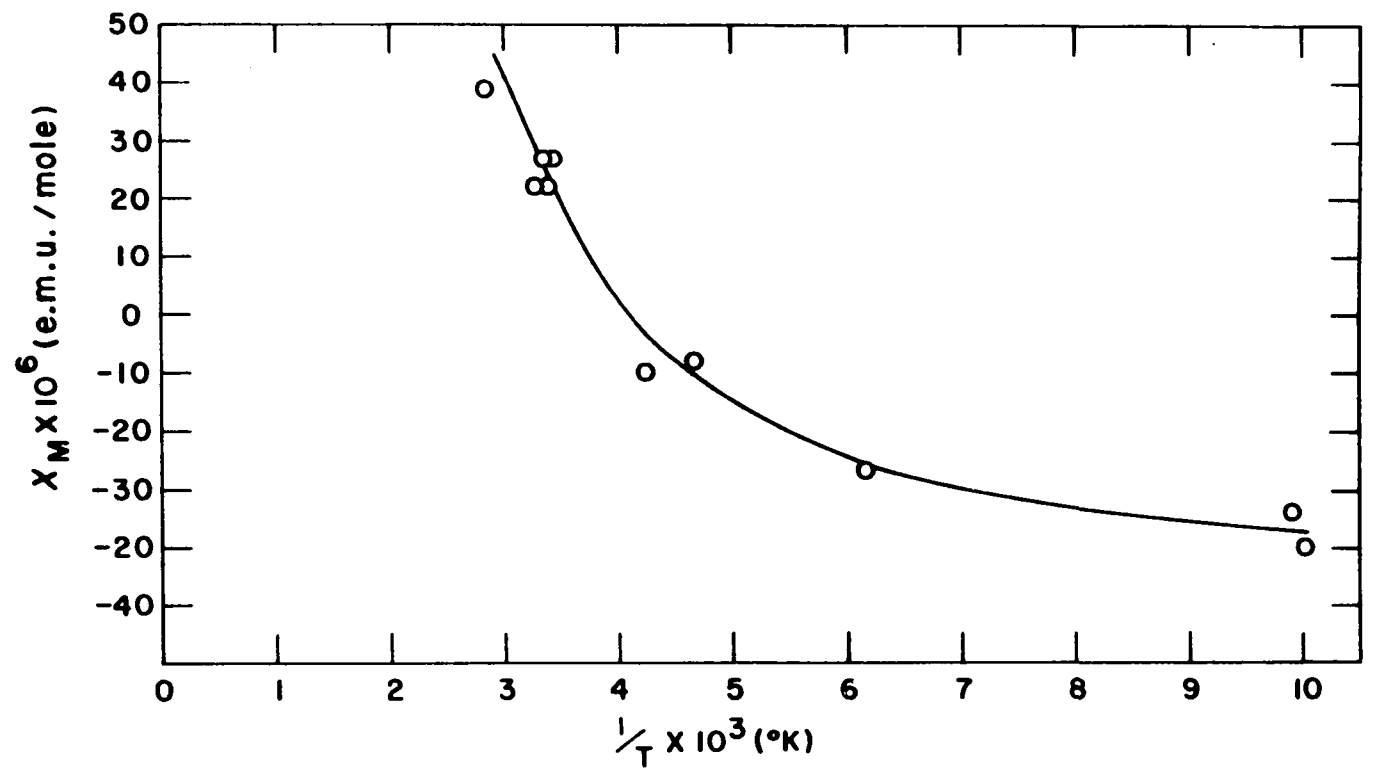
Table 6. Variation of χ_M as a function of temperature for tungsten(III) bromide

$\chi_M^a \times 10^6$ (e.m.u./mole)	T (°K)
+39	355
+22	306
+22	298
+27	297
+27	295
-10	237
- 8	214
-27	163
-34	102
-40	100

^aValues for χ_M are measured susceptibilities, uncorrected for diamagnetism of atom cores.

Tungsten(II) chloride was also observed to undergo a reaction with liquid bromine. Preliminary investigations

Figure 5. Plot of χ_M versus $1/T$ for tungsten(III) bromide



suggested the formation of a compound having the empirical formula WCl_2Br .

Anal. Calcd. for WCl_2Br : W, 54.94; X/W, 3.00.

Found: W, 54.13; X/W, 3.01 (Obtained from total halogen analysis.).

Reaction of Some Tungsten Halides with Organic Ligands

Reaction of tungsten(V) and (VI) halides with pyridine

In order to check the possible reduction of tungsten(VI) chloride with pyridine as reported previously for the reduction of the niobium(V) halides with pyridine (46), a reaction between liquid pyridine and tungsten(VI) chloride was carried out according to the procedure outlined in the experimental section. After several days at room temperature the excess pyridine was removed by distillation and the product dried on the vacuum line. From the weight gain data, mole ratios of pyridine/ WCl_6 varying from 4.64 to 4.69 were indicated. The product was light tan in color. The presence of 1-(4-pyridyl)-pyridinium chloride in the reaction mixture was identified from its characteristic behavior and UV spectrum in aqueous sodium hydroxide solution (46). The presence of this ion as one of the products indicated that reduction had taken place. The product was extracted with acetonitrile which removed the

oxidation products leaving behind the insoluble pyridine complex of tungsten. Analysis and an equivalent weight determination of this insoluble material were carried out. The results indicated the presence of a tungsten(IV) compound having the empirical formula $WCl_4(C_5H_5N)_2$. The experimental results are given in Tables 7 and 8. The reduction of tungsten in this case is understandable since reduction of the tungsten halides is generally easier than reduction of the niobium(V) halides (46). The greater tendency toward reduction exhibited by the tungsten halides is also reflected in the fact that the oxidation state of tungsten was reduced by two units, whereas that of niobium was reduced by only one unit. Thus it is to be expected that both the pentachloride and pentabromide of tungsten will undergo reduction in pyridine.

The action of pyridine on tungsten(V) chloride gave results similar to that of the hexachloride, i.e. the end product was tetrachlorodi(pyridine)tungsten(IV).

Tetrabromodi(pyridine)tungsten(IV) was prepared in a similar manner from tungsten(V) bromide and pyridine. Analysis and equivalent weight determinations of the product after extraction with acetonitrile indicated the presence of $WBr_4(C_5H_5N)_2$. The results are given in Tables 7 and 8. Mole

Table 7. Analytical results for the tetrahalodi(pyridine)tungsten(IV) complexes

Compound	% W (found)	% W (calcd.)	% X (found)	% X (calcd.)	% C ₅ H ₅ N (found)	% C ₅ H ₅ N (calcd)	X/W	py/W
WCl ₄ (C ₅ H ₅ N) ₂								
1 ^a	37.56	38.00	28.85	29.31	32.59	32.69	3.98	2.02
2 ^b	37.63	38.00	29.13	29.31	32.43	32.69	4.01	2.00
WBr ₄ (C ₅ H ₅ N) ₂								
1 ^c	27.40	27.79	47.51	48.31	23.60	23.90	3.99	2.00
2 ^b	27.52	27.79	47.83	48.31	23.82	23.90	4.00	2.01

^aPrepared by the reduction of tungsten(VI) chloride with pyridine.

^bPrepared by the reaction between tungsten(IV) halide and pyridine.

^cPrepared by the reduction of tungsten(V) bromide with pyridine.

ratios of pyridine/WBr₅ of 3.25 to 3.35 were obtained.

Table 8. Equivalent weight determinations of the tetrahalodi(pyridine)tungsten(IV) complexes

Compound	Equivalent weight (found)	Equivalent weight (calculated)
WCl₄(C₅H₅N)₂		
1 ^a	92.25	91.96
2 ^b	91.70	91.96
WBr₄(C₅H₅N)₂		
1 ^c	91.45	91.96
2 ^b	90.33	91.96

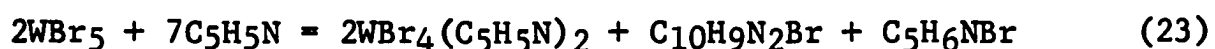
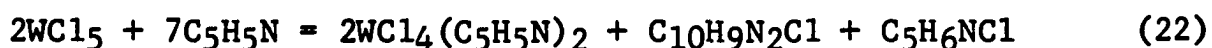
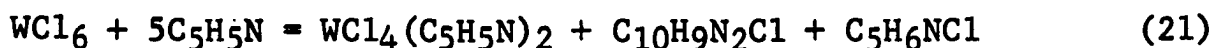
^aPrepared by the reduction of tungsten(VI) chloride with pyridine.

^bPrepared by the reaction between tungsten(IV) halide with pyridine.

^cPrepared by the reduction of tungsten(V) bromide with pyridine.

The presence of pyridinium bromide in the reaction mixture was verified from x-ray diffraction patterns. The x-ray data obtained on the tungsten(VI) chloride and pyridine reaction product were very poor and a positive identification of pyridinium chloride could not be made. Weight gain data, however, indicated that pyridinium chloride may be one of the

reaction products. From the weight gain data and the reaction products, Equations 21, 22, and 23 are proposed as possible reactions by which the reduction of the hexachloride, pentachloride, and pentabromide occur.



The reaction between tungsten(VI) chloride and pyridine in carbon tetrachloride as an inert solvent was investigated. Prasad and Krishnaiah (47) reported that pyridine reacted with the hexachloride in carbon tetrachloride to give a dark brown pyridine adduct of the hexachloride, $\text{WCl}_6(\text{C}_5\text{H}_5\text{N})_2$. Attempts to duplicate their work failed in every case and some reduction was always observed. Cooper and Wardlow (48) obtained a green insoluble $(\text{C}_5\text{H}_6\text{N})_2\text{WOCl}_5 \cdot \text{H}_2\text{O}$ complex in carbon tetrachloride even when water was excluded as much as possible. The formation of a green product in carbon tetrachloride was observed, but attempts to separate the resulting product from the oxidation products were unsuccessful. In addition, it was found that tungsten(IV) was also present in the reaction mixture. Extraction with acetonitrile separated the tungsten(IV) complex from the green material and other products.

Equivalent weight determinations on the soluble fraction after extraction with acetonitrile indicated the presence of a tungsten(V) compound. Since tungsten(IV) halides and their pyridine adducts appear to be isomorphous with the corresponding compounds of niobium(IV) and tantalum(IV), it might be expected that the monopyridine adducts of the tungsten(V) halides would also be isomorphous with those of tantalum(V). However, the x-ray pattern of the green material was not identical to that obtained for $\text{TaCl}_5(\text{C}_5\text{H}_5\text{N})$. Thus it appears that the green material either is not the monoadduct, $\text{WCl}_5(\text{C}_5\text{H}_5\text{N})$, or it is not isomorphous with the tantalum analog. Cooper and Wardlow attributed the reduction of tungsten to the presence of water and not the reducing properties of pyridine. Since they were not aware of the presence of 1-(4-pyridyl)-pyridinium chloride, no attempt was made to separate the products. Thus not much reliance can be placed in their analysis. Additional work will have to be carried out before the exact composition of this material is known. It is interesting to note, however, that the reduction is slowed down in carbon tetrachloride and provides a possible way for isolating one of the intermediates in the reduction of the hexachloride.

Reaction between tungsten(IV) halides and pyridine

The action of pyridine on tungsten(IV) chloride and tungsten(IV) bromide resulted in the formation of tan and green precipitates, respectively. The compounds were not crystalline but finely divided powders. From four to six days were required for the reactions to go to completion. This was a longer period than that required for the reduction of the higher halides with pyridine. The tetrahalodi(pyridine)tungsten(IV) compounds appeared to be exceptionally stable in air. However, when the materials were stored in closed containers after exposure to the atmosphere, the distinct odor of hydrogen halide was noticeable after several months.

Weight gain data obtained after the reaction had been completed indicated that two moles of pyridine were consumed for every mole of tungsten(IV) halide. Pyridine/WX₄ mole ratios of 1.94 and 2.14 were obtained for the tetrachloride and tetrabromide, respectively. Analytical results and equivalent weight determinations for these compounds are given in Tables 7 and 8.

X-ray diffraction data of the pyridine adducts of the tungsten tetrahalides are given in Table 9.

Table 9. X-ray diffraction data for some tetrahalodi(pyridine)-tungsten(IV) compounds

WCl ₄ (C ₅ H ₅ N) ₂		WBr ₄ (C ₅ H ₅ N) ₂	
d _{obsd.} ^a A	d _{obsd.} ^a A	d _{obsd.} ^a A	d _{obsd.} ^a A
6.43 (VVS)	2.42 (VW)	6.59 (VVS)	2.47 (W)
6.10 (VVS)	2.33 (S)	6.29 (VS)	2.40 (VS)
5.14 (VS)	2.29 (VW)	5.27 (VS)	2.36 (VVW)
4.13 (W)	2.15 (VVW)	4.20 (W)	2.20 (VVW)
3.91 (VW)	2.11 (VVW)	4.03 (VW)	2.16 (VVW)
3.82 (VS)	2.09 (VVW)	3.84 (VVS)	2.11 (VW)
3.69 (VW)		3.78 (VW)	2.03 (S)
3.64 (VW)		3.69 (VW)	2.01 (S)
3.26 (VVW)		3.20 (VS)	1.93 (W)
3.20 (VW)		2.84 (VW)	1.89 (S)
3.12 (VS)		2.70 (VVW)	1.84 (VVW)
2.79 (VW)		2.62 (VVS)	1.80 (S)
2.67 (VVW)		2.52 (S)	1.75 (S)
2.55 (S)			1.68 (W)
2.49 (W)			

^aRelative intensity values are given in parenthesis. The terms used for intensity are: V = very, W = weak, and S = strong.

The data given in Table 9 indicate that the two pyridine adducts of the tetrahalides may be isomorphous, with the tetrabromodi(pyridine)tungsten(IV) having a slightly larger unit cell. The large number of lines obtained indicates a rather complex structure. A graphical comparison of the powder patterns of the pyridine adducts of niobium, tantalum, and tungsten is given in Figures 6 and 7. These data indicate that the pyridine adducts of all three elements may be isomorphous.

Figure 6. Graphical comparison of the x-ray diffraction patterns of the di-pyridine adducts of niobium(IV), tantalum(IV), and tungsten(IV) chloride

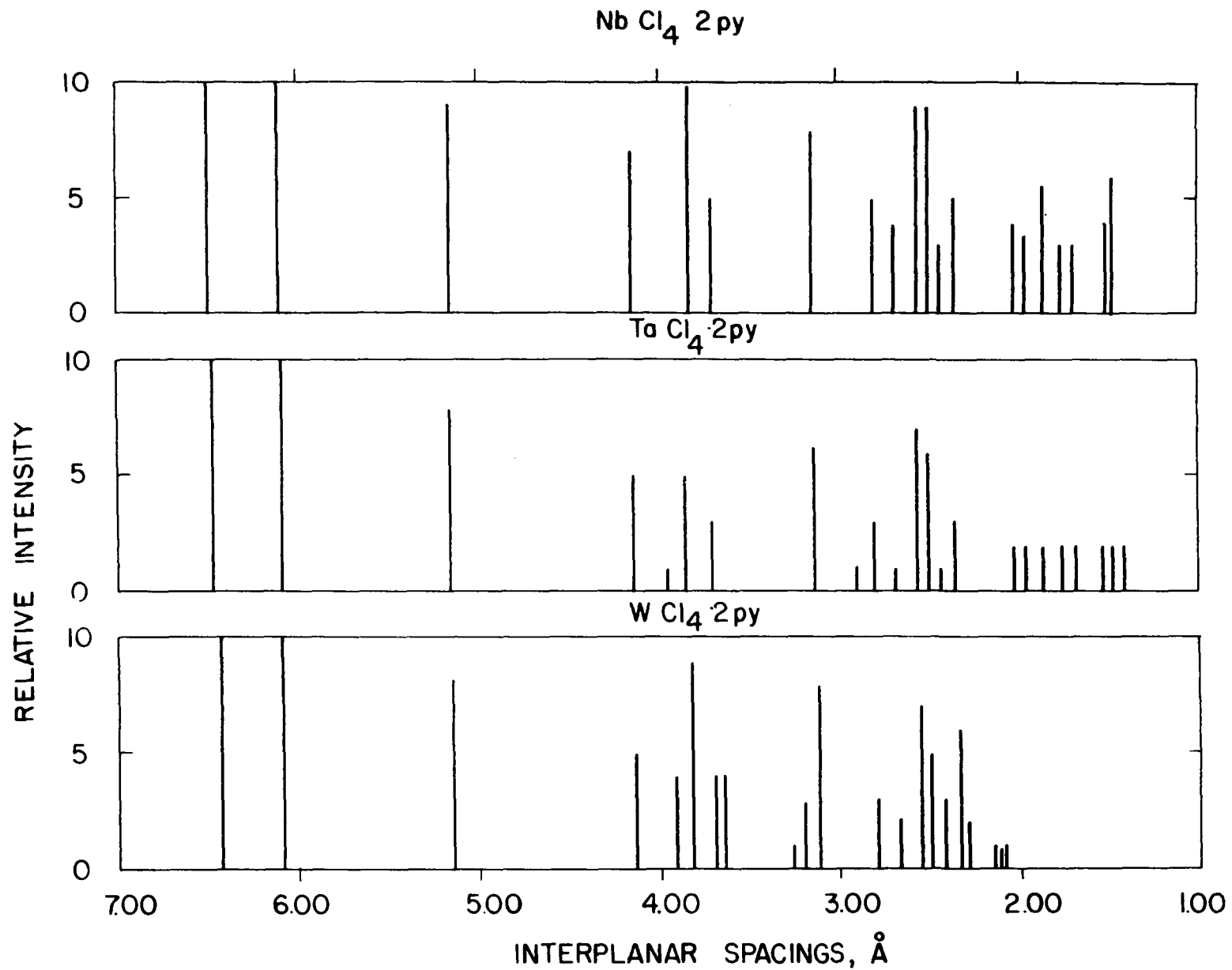
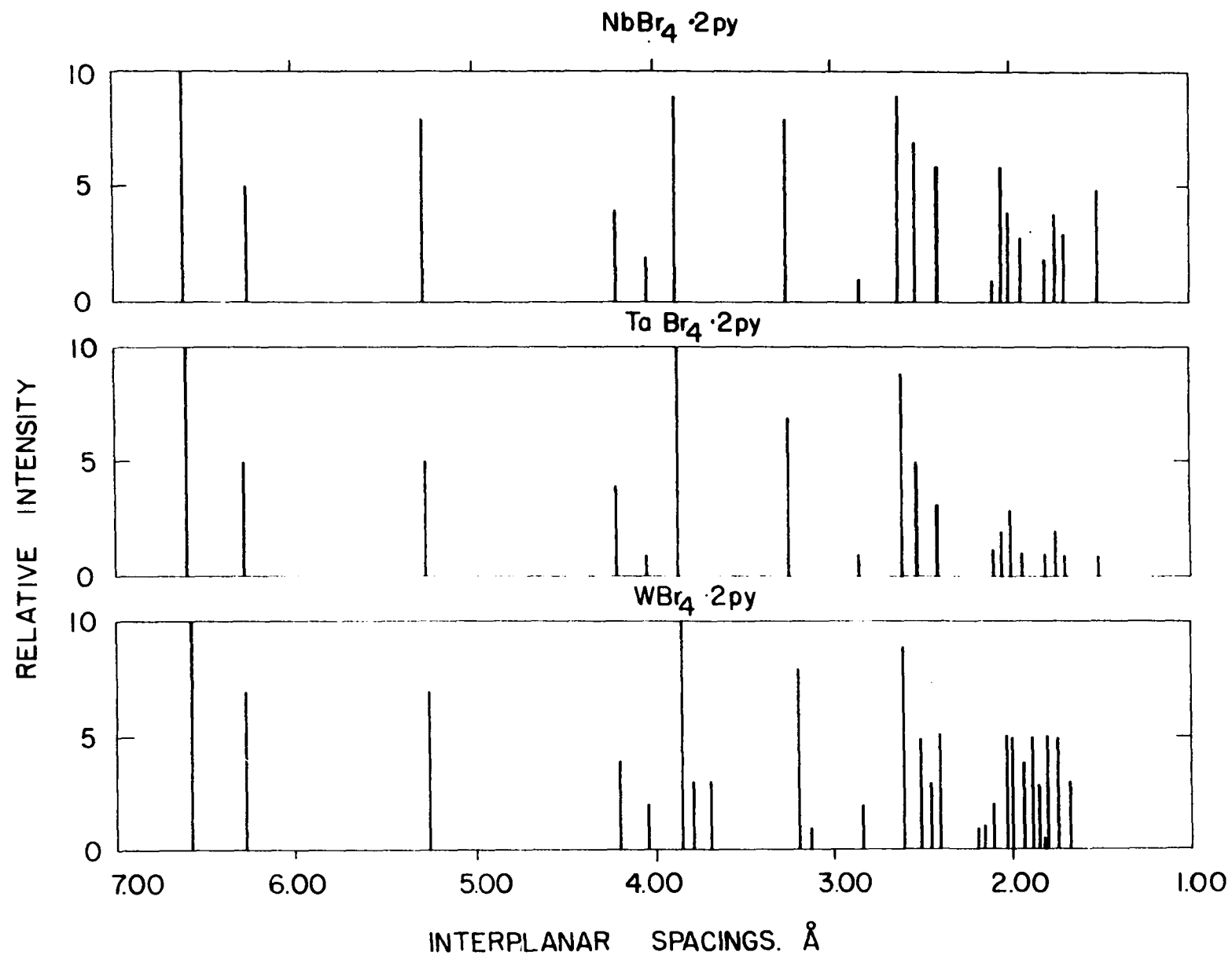


Figure 7. Graphical comparison of the x-ray diffraction patterns of the di-pyridine adducts of niobium(IV), tantalum(IV), and tungsten(IV) bromide



Reaction between Tungsten(IV) Halides
and Organic Ligands other than Pyridine

The possibility of obtaining compounds between tungsten(IV) halides and other ligands was also investigated. Ligands considered were 2,2'-bipyridine (bipy), 4-picoline (pic), and 4-ethylpyridine (etpy). These compounds were prepared by the methods outlined in the experimental section. They were analyzed for tungsten and halogen.

Anal. Calcd. for WCl_4 (bipy): W, 38.16; Cl, 29.43.

Found: W, 38.06; Cl, 29.59.

Calcd. for WCl_4 (pic)₂: W, 35.92; Cl, 27.70.

Found: W, 35.63; Cl, 27.57.

Calcd. for WCl_4 (etpy)₂: W, 34.06; Cl, 26.26.

Found: W, 35.37; Cl, 25.27.

The preparation of the alkyl pyridine derivatives became more difficult as the length of the alkyl chain was increased. Considerable difficulty occurred in preparing the 4-ethylpyridine derivative. The principle problem was in trying to remove the solvent after the preparation. On several attempts, thick, gummy products were obtained from which it was not possible to remove all of the excess solvent.

SUMMARY

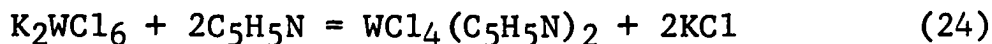
Pure crystalline tungsten(IV) chloride and tungsten(IV) bromide were prepared by a sealed tube reduction of the higher halide with aluminum in a temperature gradient. The new compound, tungsten(IV) bromide, was found to have a crystal structure and properties similar to the tetrachloride. Magnetic susceptibility measurements showed these compounds to be diamagnetic, indicating the presence of metal-metal interactions in the solid state.

The first simple trihalide, tungsten(III) bromide, was also prepared. This was accomplished by reacting tungsten(II) bromide with liquid bromine. The material was found to be thermally unstable, decomposing at temperatures greater than 80°C. It was found to be more closely related in structure and properties to the dibromide, rather than the higher tungsten bromides.

Tungsten(II) chloride and bromide were prepared in a pure state by the disproportionation of the respective tungsten tetrahalide. The principle advantage of this method is the recovery of the higher halide which is a by-product of the reaction. This higher halide may be obtained in pure form by several repeated sublimations to remove trace amounts of

tetrahalide.

The reaction of the hexachloride, pentachloride, and pentabromide of tungsten with pyridine is interesting since it provides an alternative path to the preparation of the pyridine adducts of tungsten(IV) chloride and tungsten(IV) bromide, respectively. The tetrahalodi(pyridine)tungsten(IV) compounds were also prepared by reacting the respective tungsten tetrahalide with excess pyridine. A recent communication with Fowles¹ indicated that tetrachlorodi(pyridine)-tungsten(IV) could also be obtained from potassium hexachlorotungstate(IV) and pyridine as illustrated in Equation 24. This reaction was also reported by Kennedy and Peacock (49).



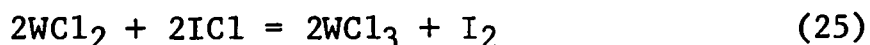
X-ray diffraction data indicated the structure of these solid addition compounds to be complex. It does appear, however, that they were isomorphous with each other and with the pyridine addition compounds of niobium and tantalum.

The tungsten(IV) halides were found to be good coordinating agents forming stable complexes with 2,2'-bipyridine, 4-picoline, and 4-ethylpyridine.

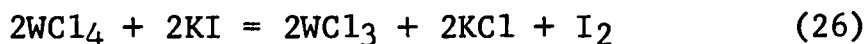
¹Fowles, G. W. A., Southampton University, Southampton, England. On the preparation of tetrahalodi(pyridine)tungsten(IV) complexes. Private communication. 1963.

SUGGESTIONS FOR FUTURE WORK

The preparation of tungsten(III) bromide represents only an introduction to a study of the simple trihalides. The other tungsten(III) halides (fluoride, chloride, and iodide) have not as yet been prepared. The preparation of these compounds is necessary in making a complete study of the properties of the trihalides. The reaction of tungsten(II) iodide with liquid iodine is a good first attempt for the preparation of tungsten(III) iodide. Suggestions for the possible methods of preparing tungsten(III) chloride include: (1) the reaction between tungsten(II) chloride and liquid chlorine; (2) the action of iodine monochloride on tungsten(II) chloride as illustrated in Equation 25; (3) the reduction of a higher



chloride such as tungsten(IV) chloride with potassium iodide as illustrated in Equation 26.



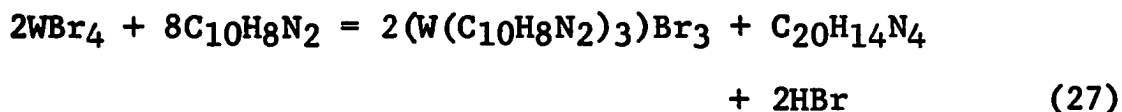
Further studies on the properties of tungsten(IV) bromide would help to elucidate the entire tungsten bromide system. Vapor pressure and dissociation pressure measurements would clarify the conditions required for the synthesis of this compound.

Isolation and identification of the green product obtained in the reaction between tungsten(VI) chloride and pyridine in carbon tetrachloride would be beneficial. This material apparently is an intermediate in the reduction of the hexachloride. Knowledge of its composition would be of value in determining the reduction mechanism for this reaction.

The extension of the reaction between tungsten(IV) halides and ligands other than pyridine indicated that the tetrahalides are good coordinating compounds. Preliminary investigations were carried out on trimethylamine, triethylamine, N,N,N',N'-tetramethylethylenediamine. The triethylamine and N,N,N',N'-tetramethylethylenediamine appeared to form monoadducts. This study could be extended to other ligands such as 3,5-lutidine, 2,6-lutidine, 3-picoline. It is possible that one of these compounds may be sufficiently soluble to obtain molecular weight and dipole moment measurements. Knowledge of these properties would help in the study of the structure of these compounds. Additional uses for these compounds are discussed in Part II of this dissertation.

Initial studies of the action of 2,2'-bipyridine on tungsten(IV) bromide under conditions similar to those used to prepare WCl_4 (bipy) were interesting. The compound WBr_4

(bipy) was expected, however, an equivalent weight determination indicated the presence of a tungsten(III) compound. The analysis for tungsten and bromide was considerably lower than that expected for the predicted compound. Burstall (50) observed that certain ruthenium compounds underwent reduction in the presence of 2,2'-bipyridine. Thus tungsten(IV) bromide might be expected to undergo a similar reduction according to Equation 27.



$\text{C}_{10}\text{H}_8\text{N}_2$ is 2,2'-bipyridine; the product $\text{C}_{20}\text{H}_{14}\text{N}_4$ is a tetramine. Additional work should be carried out on this reaction to separate the products. This would give a tungsten(III) compound surrounded by a symmetrical field. This material should have interesting spectral and magnetic properties.

**PART II: SPECTROPHOTOMETRIC AND SUSCEPTIBILITY STUDIES OF
SOME TUNGSTEN(IV) COMPLEXES**

REVIEW OF PREVIOUS WORK

In recent years the unusual magnetic behavior and spectra of the transition metal complexes have been explained in terms of the ligand (crystal) field theory. Although this theory has been successful in explaining many of the properties of the first transition series, considerable difficulty has occurred in trying to match theory with the experimental data of the second- and third-row transition elements. This is due to the rather large differences which exist between $3d^n$ transition metal complexes and those containing $4d^n$ and $5d^n$ electrons. These differences exist because the 4d and 5d electrons are less tightly bonded to the metal atom than are the 3d electrons. Thus molecular-orbital formation occurs readily, $10 D_q$ is increased, and the "charge-transfer" states have lower energy than most "crystal-field" states (51, p. 273). The spin-orbit coupling constant, ξ_{n1} , usually omitted in calculations involving 3d-transition elements becomes important since $\xi_{5d} \sim 2 \xi_{4d} \sim 5 \xi_{3d}$ (52, p. 292). The expected results are not always obtained and the interpretation becomes increasingly difficult.

Very little work has been done on the tungsten(IV) complexes, previous work being concerned primarily with the

octacyanotungstate(IV) compounds. This apparent lack of work is due primarily to the difficulty with which these compounds are obtained. The d^2 complexes become less stable with regard to oxidation by the air and hydrolysis on going from the first to the third transition row elements. Recently, however, the preparation of M_2WX_6 and $WX_4(C_5H_5N)_2$ ($M = K, Rb, Cs$; $X = Cl, Br$) was reported (49). The work presented in this section was performed to provide an introduction into the study of d^2 compounds of the third-row transition elements.

EXPERIMENTAL

Materials

Complexes

The compounds $WCl_4(C_5H_5N)_2$, $WBr_4(C_5H_5N)_2$, and $WCl_4(bipy)$ were prepared and stored as outlined in Part I of this dissertation. K_2WCl_6 was prepared by reacting stoichiometric amounts of tungsten(IV) chloride and potassium chloride in a sealed vycor tube at $800^\circ C$. for one hour.

Solvents

To insure complete removal of all water from the solvent, acetonitrile or pyridine, the following method of drying was used. The solvent was first dried over molecular sieves which had been outgassed at $300^\circ C$. to ca. 10^{-5} Torr for twenty-four hours. The solvent then was distilled onto previously outgassed calcium hydride. After twenty-four hours, the solvent was frozen in a Dry Ice-acetone bath, outgassed to ca. 10^{-5} Torr, and stored over calcium hydride until used.

Analysis

For solutions containing only small amounts of tungsten, the procedure reported by Norwitz (53) was used. The method was based on the formation of a colored complex between

tungsten(V) and thiocyanate ion in a strong acid media. The solution to be analyzed was evaporated to dryness to remove excess solvent. Nitric acid was added to oxidize the tungsten to tungsten(VI). The solution then was made alkaline with sodium hydroxide and digested to remove pyridine. Sulfuric acid was added, and the solution was evaporated to fumes of sulfur trioxide. The resulting solution or an aliquot thereof was placed in a fifty milliliter volumetric flask. Concentrated hydrochloric acid was added to put the tungsten into true solution. Stannous chloride was added for reduction of the tungsten to the plus five oxidation state. The addition of sodium thiocyanate solution resulted in the formation of a yellow solution which varied in intensity depending on the tungsten content. The optical density of the solutions was read from a Beckman Model DU spectrophotometer at 400 m μ . The color resulting from complex formation obeyed Beer's law up to thirty milligrams of tungsten in the original volume.

Measurements

Conductivity

The electrolytic conductance of the tetrahalodi(pyridine)-tungsten(IV) complexes in pyridine was determined. The conductance apparatus which consisted of an all glass cell connected

to a mixing chamber through a fritted disk is shown in Figure 8. Platinum electrodes were sealed into the cell in such a way that the cell was vacuum tight. These electrodes were square, 18 mm. on an edge and 8 mm. apart. The mixing chamber was connected to the vacuum system through a ball and socket joint and a stopcock. A Leeds and Northrup AC conductance bridge, Model 4866-60 was used for all conductance measurements. The conductance was measured at 20°C. by placing the cell in a constant temperature water bath.

The conductance vessel was thoroughly outgassed, loaded with the di-pyridine adduct, and evacuated to ca. 10^{-5} Torr. Pyridine was distilled into the conductance cell, and the apparatus was sealed off from the system. For use as a reference value, the conductivity of the solvent was determined at 20°C., and the conductance was calculated from Equation 28.

$$K = k(1/R) \quad (28)$$

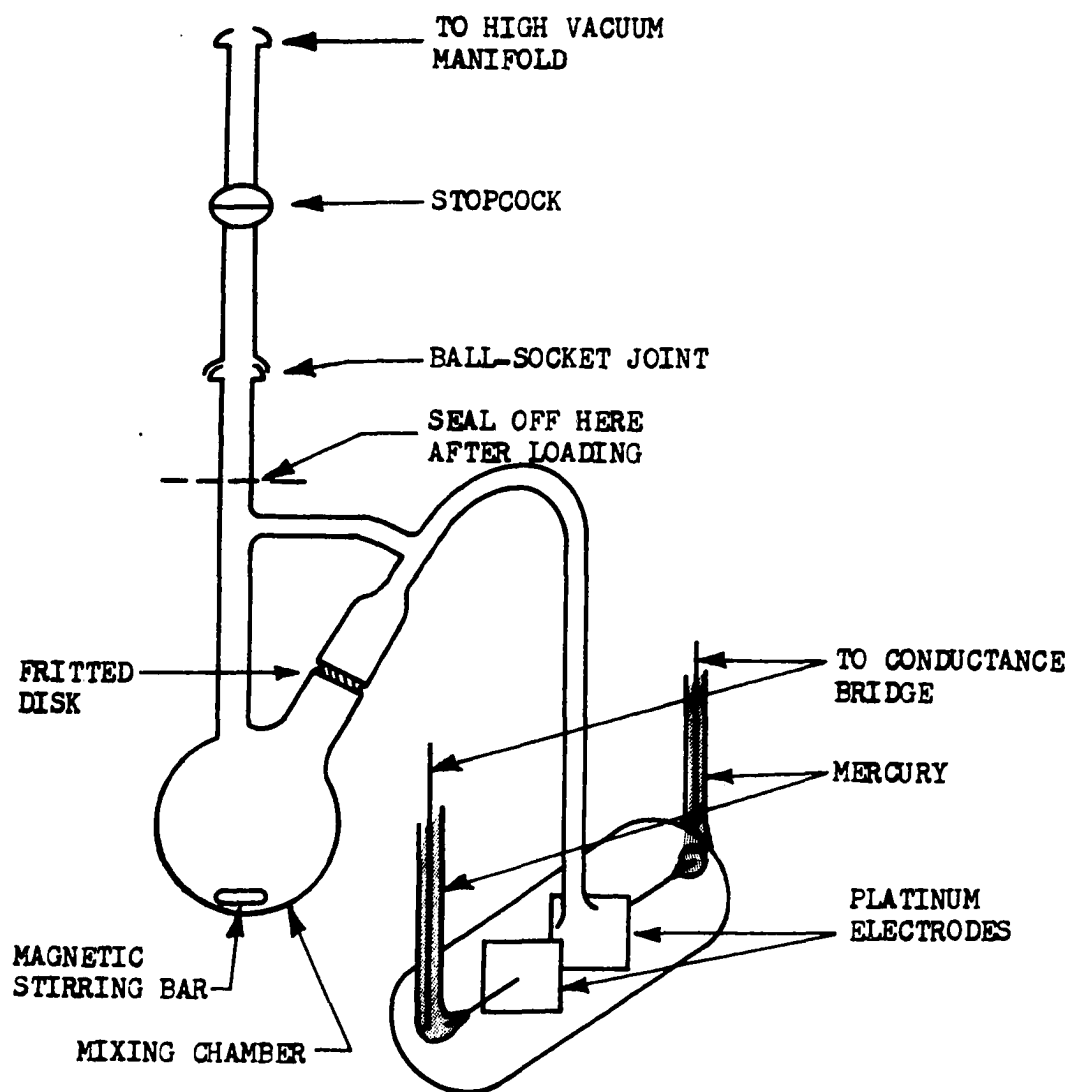
Where: K = specific conductance in $\text{ohm}^{-1} \text{ cm.}^{-1}$,

k = cell constant in cm.^{-1} ,

R = resistance of solution in ohm.

The liquid then was decanted onto the compound whose conductivity was to be determined. After some of the compound had dissolved, the solution was filtered into the electrode

Figure 8. Conductance cell



chamber, and its specific conductance was determined at 20°C. after equilibrating in a constant temperature bath.

For those solutions that showed conductivity, the equivalent conductivity was calculated from Equation 29.

$$\Lambda = 1000 (K/C) \quad (29)$$

Where: Λ = equivalent conductance in $\text{cm.}^2 \text{ eq.}^{-1} \text{ ohm}^{-1}$,

K = specific conductance in $\text{ohm}^{-1} \text{ cm.}^{-1}$,

C = concentration of the solution in g. eq./l.

The concentration of the solution whose conductance was measured was determined by analyzing the solution for tungsten and determining the volume of solution in the conductivity cell.

Visible- and ultraviolet-absorption spectra

The visible spectra of various tungsten(IV) complexes were determined in the region 300 to 700 m μ using a Cary 14 recording spectrophotometer. The apparatus used was similar to that described by McCarley and Torp (35). To insure that the vessel was free from moisture, it was dried in an oven at 120°C. for one day and then outgassed on the vacuum line to ca. 10^{-5} Torr for an additional day.

The sample was placed in the mixing chamber in the dry box. The apparatus then was connected to a vacuum system and

outgassed. The solvent was distilled onto the sample, and the vessel was sealed off from the rest of the system. By alternately filtering and distilling the solution between the mixing vessel and the cell, a suitable concentration was obtained which gave peaks in the range of the spectrophotometer. The spectra of the solutions were determined using pure solvent as a reference. Time studies were made on each complex.

The visible- and ultraviolet-absorption spectra of the solid tungsten(IV) complexes were obtained using a Beckmann DU spectrophotometer with a diffuse reflectance attachment. To increase the intensity of the absorption bands, the samples were diluted with magnesium carbonate.

Magnetic susceptibility

The magnetic susceptibility of the tetrahalodi(pyridine)-tungsten(IV) complexes was obtained by the method outlined in Part I of this dissertation.

RESULTS AND DISCUSSION

Conductance Study of the Tetrahalodi(pyridine)-tungsten(IV) Complexes in Pyridine

A conductance study of the tetrahalodi(pyridine) tungsten(IV) complexes in pyridine was made to determine whether or not ionic species were present in solution. The results are given in Tables 10 and 11.

Table 10. Conductance of the tetrahalodi(pyridine) tungsten(IV) complexes in pyridine as a function of time

$WCl_4(C_5H_5N)_2^a$		$WBr_4(C_5H_5N)_2^b$	
Time (hours)	Conductance $\times 10^6$ (ohm^{-1})	Time (hours)	Conductance $\times 10^6$ (ohm^{-1})
pure pyridine	less than 10^{-7}	pure pyridine	less than 10^{-7}
3.67	8.06	4.00	4.32
7.25	8.12	14.00	4.92
23.33	8.34	22.00	5.20
29.25	8.43	37.75	5.47
42.25	8.54	45.00	5.52
55.00	8.59	57.00	5.56 ^c
72.00	8.62		
90.00	8.64 ^c		

^aConcentration of 2.88×10^{-4} g. eq. W/l.

^bConcentration of 1.32×10^{-4} g. eq. W/l.

^cLimiting value.

Table 11. Conductance studies of the tetrahalodi(pyridine)tungsten(IV) complexes in pyridine at 20°C.

Solution	K_{pyridine} (ohm ⁻¹ cm ⁻¹)	K_{solution} (ohm ⁻¹ cm ⁻¹)	Concentration (g. eq. W/l)	$\sqrt{\kappa}$ (cm ² eq. ⁻¹ ohm ⁻¹)
WCl ₄ (C ₅ H ₅ N) ₂	less than 10 ⁻⁷	1.62 x 10 ⁻⁵	2.88 x 10 ⁻⁴	56.5
WBr ₄ (C ₅ H ₅ N) ₂				
1	less than 10 ⁻⁷	0.787 x 10 ⁻⁵	0.792 x 10 ⁻⁴	99.4
2	less than 10 ⁻⁷	1.05 x 10 ⁻⁵	1.32 x 10 ⁻⁴	79.5
3	less than 10 ⁻⁷	3.12 x 10 ⁻⁵	7.28 x 10 ⁻⁴	42.6

The resistance of the pure pyridine was greater than the maximum resistance of the bridge and could not be measured. From Table 11, it appears that the tetrahalodi(pyridine)-tungsten(IV) complexes become electrolytes in pyridine solution. The values obtained for the equivalent conductance fall in the range ($\Lambda_0 = 48.0$ to $102.2 \text{ cm.}^2 \text{ eq.}^{-1} \text{ ohm}^{-1}$) of univalent electrolytes in pyridine (54, p. 125). Examination of Table 10 indicates that the solids do not exist as electrolytes but undergo ionization in the solvent over a period of time. Discussion of the possible species in solution will be given after presentation of the absorption data in the following paragraphs.

Absorption Spectra of some Tungsten(IV) Halide Complexes

The absorption spectra of the tetrahalodi(pyridine)tungsten(IV) complexes and tetrachloro(2,2'-bipyridine)tungsten(IV) were determined in the visible region as described in the experimental section. These experiments were initiated to further the study of the type of bonding and the structure of these compounds. The spectra of the compounds were examined both in the solid and in solution (cf. Table 12 and Figures 9 thru 11). For comparison, the values reported by Kennedy and Peacock (49) are also given.

Table 12. Visible- and ultraviolet-absorption maxima of some tungsten(IV) halide complexes

Compound	State	Absorption peaks (m μ) (ϵ_{\max} in parenthesis) ^f				
WCl ₄ (C ₅ H ₅ N) ₂	solid - 1	488	375	320	255	
		2 ^a	---	380	327	260
	pyridine - 1 ^b solution	510(1300)	380(2360)	---	---	---
		1 ^c	516(5470)	---	320	---
		2 ^b	510(1280)	380(2550)	---	---
		2 ^c	516(5580)	---	320	---
WCl ₄ (bipy)	solid	520	412.5 ^e	330		
	CH ₃ CN soln	510(1060)	412.5 ^e (700)			
WBr ₄ (C ₅ H ₅ N) ₂	solid - 1	495	445	410	330	310
		2 ^a	---	450	410	332
	pyridine solution	512(1170) ^b	442(4250) ^b	403(5500) ^b	328 ^c	308 ^c

^aData of Kennedy and Peacock.

^bSpectrum observed immediately after solution of complex.

^cSpectrum observed after solution did not appear to undergo any further changes.

^dAbsorption off scale due to high concentration of solution.

^eShoulder.

^f ϵ_{\max} values are ± 50 l mole⁻¹cm⁻¹.

Figure 9. Absorption spectra of tetrachlorodi(pyridine)tungsten(IV) and potassium hexachlorotungstate(IV). $\text{WC1}_4(\text{C}_5\text{H}_5\text{N})_2$ in pyridine solution = 1.6×10^{-4} molar

Curve 1 - two hours after solution in pyridine

Curve 2 - 14.5 hours after solution in pyridine

Curve 3 - 25 hours after solution in pyridine

Curve 4 - Reflectance spectrum of solid $\text{WC1}_4(\text{C}_5\text{H}_5\text{N})_2$
(Units of absorbance are arbitrary)

Curve 5 - Reflectance spectrum of solid $\text{K}_2\text{WC1}_6$
(Units of absorbance are arbitrary)

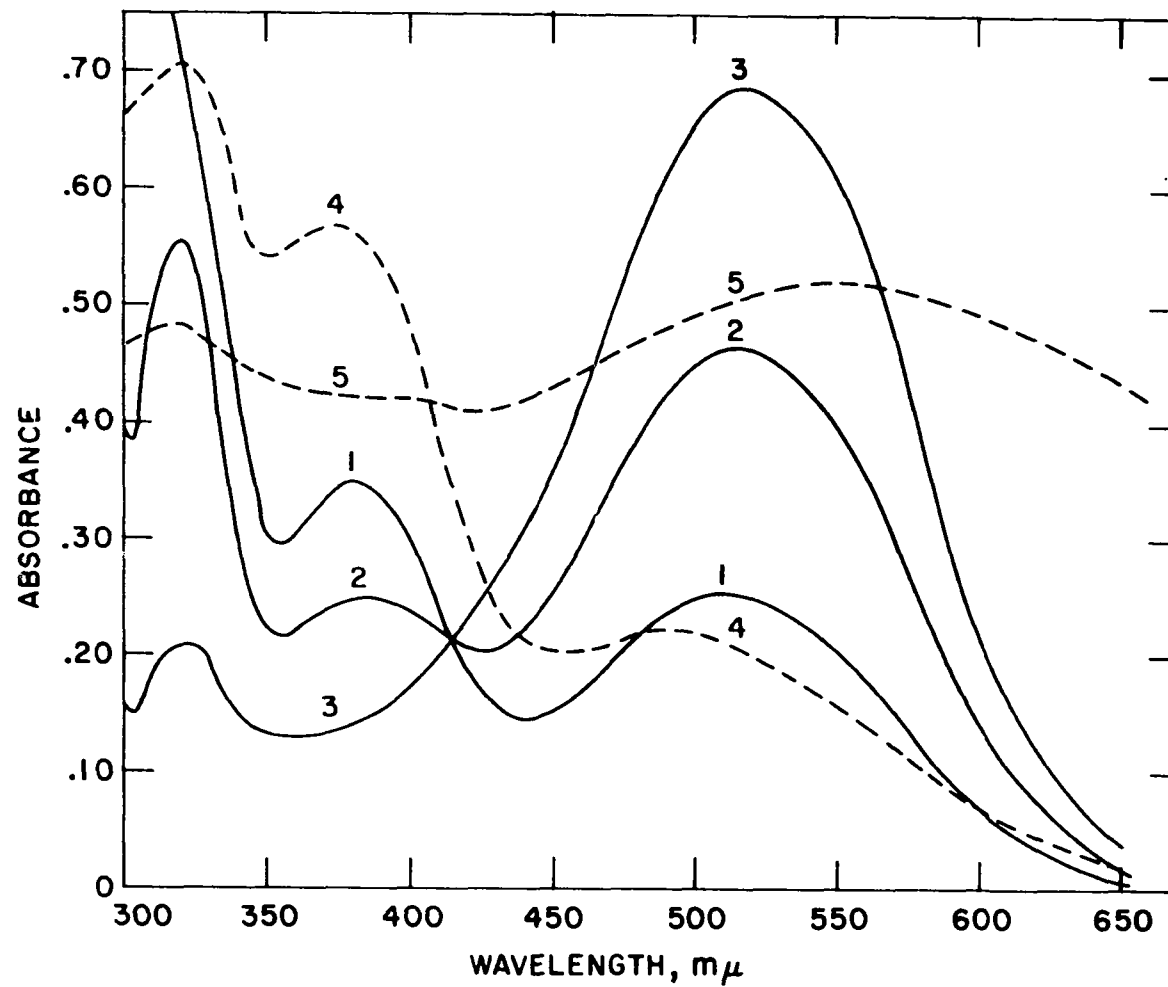


Figure 10. Absorption spectra of tetrabromodi(pyridine)tungsten(IV).
 $C_{WBr_4(C_5H_5N)_2}$ in pyridine solution = 1.2×10^{-4} molar

Curve 1 - 1.25 hours after solution in pyridine

Curve 2 - 4.75 hours after solution in pyridine

Curve 3 - 20 hours after solution in pyridine

Curve 4 - 34 hours after solution in pyridine

Curve 5 - Reflectance spectrum of $WBr_4(C_5H_5N)_2$
(Units of absorbance are arbitrary)

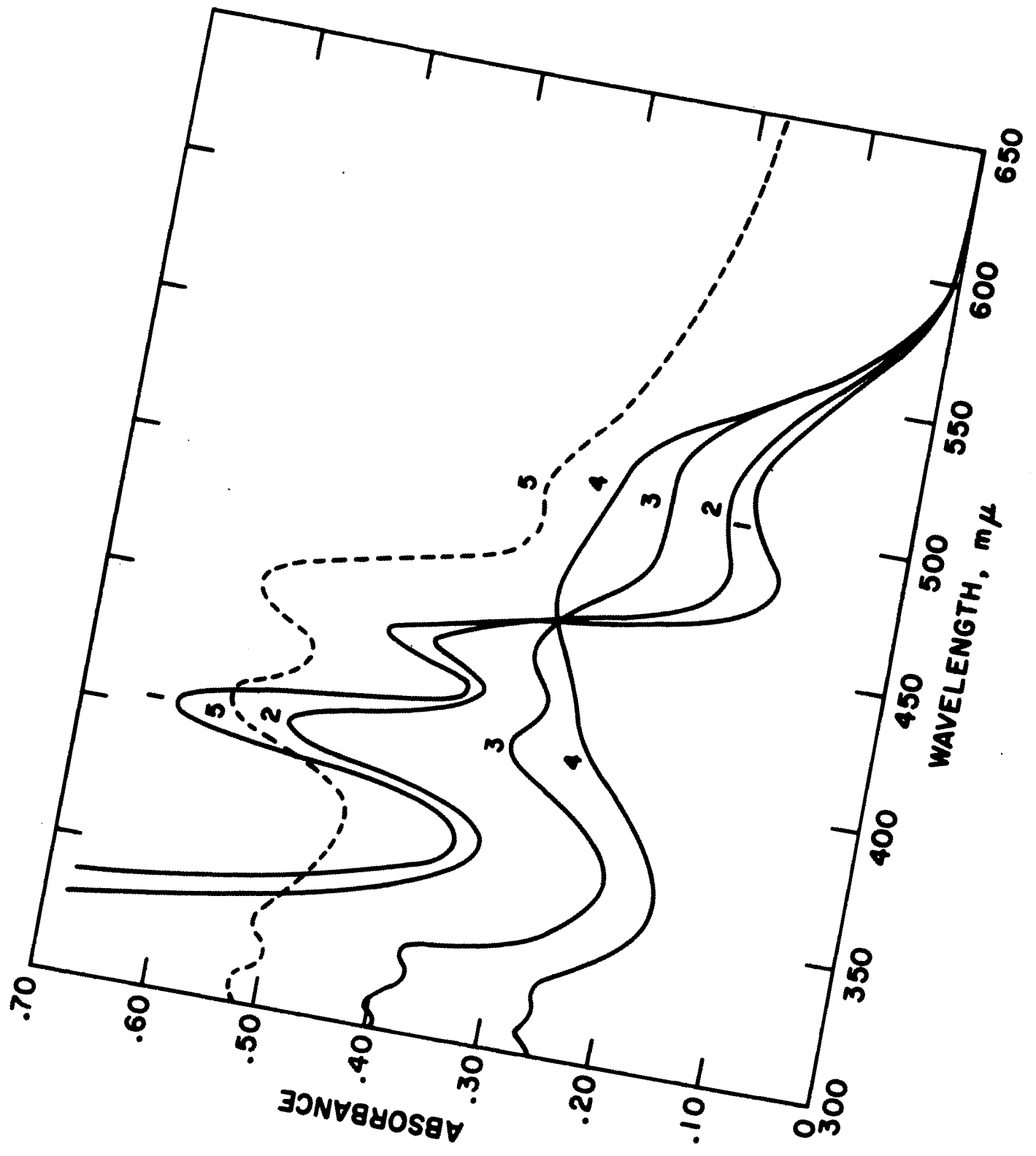
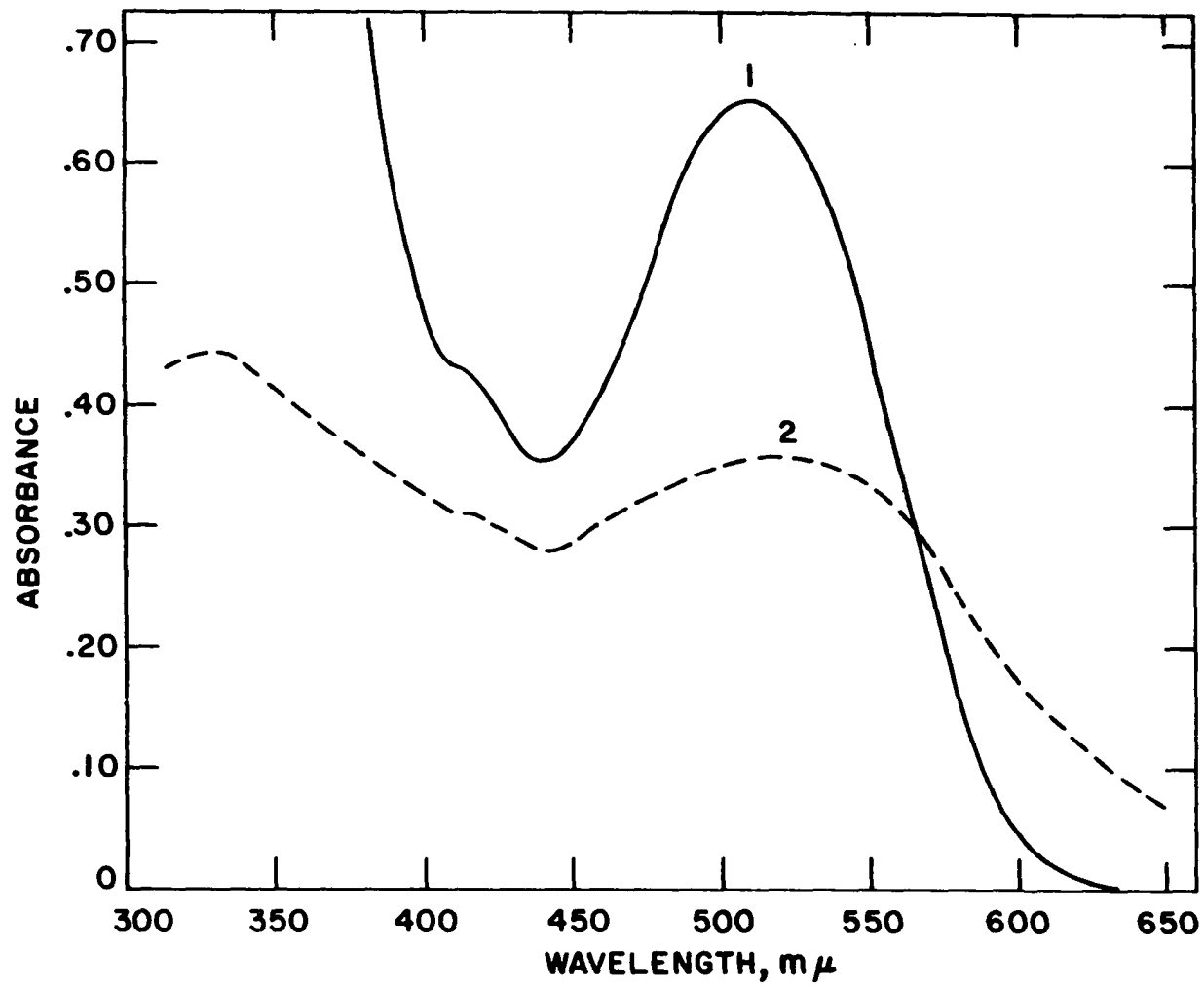


Figure 11. Absorption spectra of tetrachloro(2,2'-bipyridine)tungsten(IV).
 $C_{WCl_4(bipy)}$ in acetonitrile = 6.2×10^{-4} molar

Curve 1 - Stable spectrum in acetonitrile solution

Curve 2 - Reflectance spectrum of solid $WCl_4(bipy)$
(Units of absorbance are arbitrary)

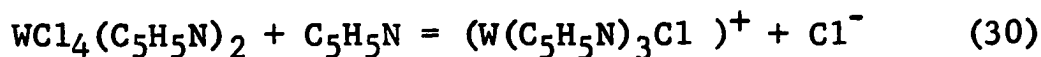


The solution of tetrachloro(2,2'-bipyridine)tungsten(IV) was found to be stable for at least three days in acetonitrile. Solutions of the tetrahalodi(pyridine)tungsten(IV) complexes in pyridine when kept in sealed spectroscopy cells were not stable. Figures 9 and 10 show that these compounds undergo changes during the first forty-eight hours. After this initial change, they become stable. Hydrolysis of the complex can be ruled out for two reasons. First, the cells were carefully treated as outlined in the experimental section to remove moisture. If residual moisture was present, the tetrachloro(2,2'-bipyridine)tungsten(IV) complex would not have shown the stability that it did. Secondly, an experiment was performed in which a trace of moisture was purposely admitted into one of the cells. There was no comparison between the spectrum of the resulting solution and that of the compound in dry pyridine.

The following discussion will be concerned with the species present in the pyridine solution of $WCl_4(C_5H_5N)_2$ although it applies equally well to the pyridine solution of $WBr_4(C_5H_5N)_2$. It is evident that one species, absorbing at 380 and 510 $m\mu$ is converted to another species, absorbing at 516 $m\mu$ (cf. Curves 1 thru 3, Figure 9). In the case of

$WBr_4(C_5H_5N)_2$, the initial species absorbing at 403, 442, and 512 $m\mu$ is converted to another species absorbing at ca. 515 $m\mu$ (cf. Curves 1 thru 4, Figure 10). This is evident by the presence of an isosbestic point at 415 $m\mu$ and 456 $m\mu$ for the chloride and bromide complexes, respectively. Two possible modes by which this change may take place will be considered. These are: (1) the formation of an electrolyte; and (2) a trans to cis isomerization.

The high conductance of the material in pyridine solution indicates the formation of an electrolyte. One possible mode of ionization of the simple adduct in pyridine solution is illustrated in Equation 30.



The formation of this ion would also account for the change observed in the spectrum of the di-pyridine adduct in pyridine solution. From Equation 30 it would appear that if an excess of chloride ion was present, the reaction should be slowed down or even prevented. A time study of a solution of $WCl_4(C_5H_5N)_2$ in pyridine saturated with lithium chloride was carried out. Although the spectrum of this solution underwent a change similar to that observed without lithium chloride, a considerably longer time was required for this change

to come about. Thus although the reaction was not prevented, it is evident that the chloride ion plays an important role in the reaction which these di-pyridine adducts undergo.

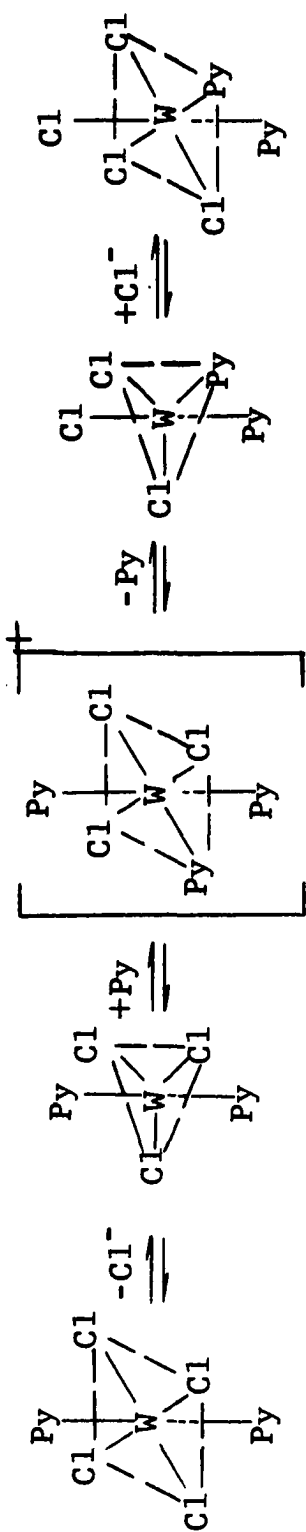
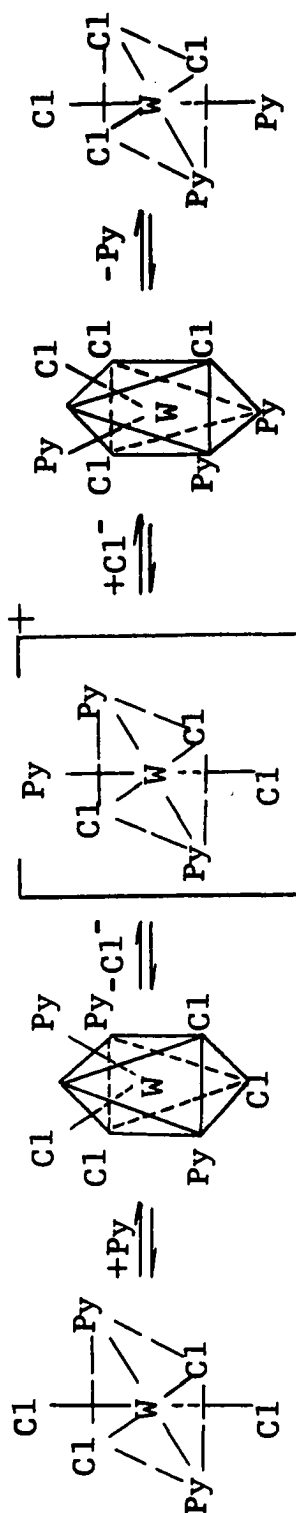
The change observed in the spectrum may also be accounted for by a trans to cis isomerization. To begin with, let it be assumed that the initial species is of the trans configuration. Comparison of the spectra of the initial solution species and the solid (cf. Curves 1 and 5, Figure 9) indicates that the same configuration is present in both. The trans form of these complexes should be more stable than the cis isomer because of steric hindrance between adjacent ligands in the latter. On the other hand, the formation of a cis configuration in solution is favorable since the arrangement of ligands would result in a net dipole moment for the molecule. This would result in a greater energy of solvation than would be exhibited by the trans form in a polar solvent such as pyridine.

Two types of reaction sequence may bring about this isomerization. One is the S_N1 dissociation of an octahedral complex to give a five coordinate structure which adds a new ligand from solution. The other is the S_N2 attack on an octahedral ion by a seventh ligand followed by expulsion of

one of the original ligands. It is not possible from the data obtained to determine by which path the reaction would proceed. The following conclusions can be drawn, however, from existing data: (1) the formation of a five or seven coordinate species as the only intermediate is improbable since these species have only a momentary existence (55, p. 95) and the conductivity data indicate the presence of a stable ionic species; (2) the reaction does not go to completion. Curve 4, Figure 10 is the spectrum of the stabilized solution. Comparison between this spectrum and that of the initial solution species (cf. Curve 1, Figure 10) indicates the presence of some of the initial species and thus it appears that the end result is an equilibrium mixture.

The reaction which may take place by a S_N1 or S_N2 mechanism is shown in Figure 12. The formation of a pentagonal bipyramid in the S_N1 process and the cis attack in the S_N2 process is arbitrary. These are not necessarily the only mechanisms available. The ion $(W(C_5H_5N)_3Cl_3)^+$ could be formed equally well from a tetragonal pyramid in the S_N1 process or by a trans attack in the S_N2 process. In addition, no distinction is made as to whether a 1,2,6- or 1,2,3- $(W(C_5H_5N)_3Cl_3)^+$ isomer is formed. Additional experimental work will

Figure 12. Suggested rearrangement of the tetrachlorodi(pyridine)-tungsten(IV) complexes in pyridine by a S_N1 or S_N2 process

 S_N1  S_N2

have to be carried out before these additional distinctions can be made.

The formation of the $(W(C_5H_5N)_3Cl_3)^+$ species stable in pyridine solution gives a reasonable explanation for the observed conductance of the di-pyridine adducts. Whether an equilibrium exists between the initial (trans) species and this ionic species or the reaction continues to yield the cis product in solution cannot be said with great certainty. Although the final spectrum may be attributed to the ionic species, the formation of a cis isomer cannot be ruled out for the following reasons. (1) The appearance of the peak in the final spectrum at 516 $m\mu$ (cf. Curve 3, Figure 9) is in the same vicinity as the peak obtained for the 2,2'-bipyridine adduct of tungsten(IV) chloride at 510 $m\mu$ (cf. Curve 1, Figure 11) which has to be a cis compound. (2) The intensity of this band increases as the new species grows in. It is often found that the cis compound has more intense bands than the trans compound (56, p. 191). (3) The addition of excess chloride did not stop the reaction from occurring although it did slow it down. This alone, however, is not sufficient evidence that the ionic species is the end product of the reaction. Thus the only conclusion which can be drawn at this time is that an

equilibrium exists between the initial and ionic species or between the trans, cis, and ionic species in pyridine solution.

Since the final solution in the case of the tetrahalo-di(pyridine)tungsten(IV) complexes apparently contains two species, assignment of electronic transitions is not possible. However, comparison between the spectra of the solid and initial solution indicates that the species goes into solution in a form originally present in the solid, presumably the trans isomer. To elucidate the difficulties which arise in trying to assign electronic transitions, the following brief summary is presented.

Most of the complexes of the transition metals show two distinct kinds of absorption of light: those which can be considered as taking place within the d-shell of the ion, and those due to charge-transfer processes (57). The first kind is due to transitions involving only electrons on the central metal atom, primarily the electrons associated with the d-orbitals of the isolated metal atom. These are called d-d transitions. It is these transitions which are responsible for the usual colors associated with complex ions. Transitions of this kind occur chiefly in the visible, and may

extend into the ultraviolet and infrared regions of the spectrum. The intensities of bands occurring from d-d transitions are low, having molar extinction coefficients generally below 200 (58, p. 101). The second kind of absorption occurs chiefly in the ultraviolet, but sometimes extends into the visible. These absorptions are referred to as charge transfer and they have considerably higher intensities with molar extinction coefficients generally above 2000 (58, p. 101). This phenomenon is the characteristic feature of an electron being transferred from one definite part of the system to another when light is absorbed. Such spectra are characteristic of associated pairs of molecules, where one can identify a charge-donating group and a charge-accepting group (55, p. 372). When the interaction between the metal ion and the ligands becomes particularly strong, the two types of transitions are no longer even approximately distinct and the theoretical treatment is then more complicated (57).

The general theory concerning d-d spectra utilizes the "crystal field" method of Bethe (59). Essentially the theory states that the five d-orbitals of a transition metal ion, which are degenerate and equal in energy in an isolated, gaseous atom, are split into orbitals of different energy by the

electrostatic fields created by the ligands. Thus for an ion with an unfilled d-shell, transitions can occur between these levels of different energy. Normally, only those ions or molecules directly attached to the metal atom are important in determining the structure of the energy-level scheme of the ion. Thus the general features of the spectrum of a complex ion in solution are similar to those of the same ion in a crystal (58).

The degree of splitting is calculated from the quantum mechanical perturbation theory. Since the unperturbed wave functions are not known exactly and since the true value of the perturbing electric field is not known, it is not possible to make exact calculations. Nevertheless, semiquantitative information can be obtained from these approximate calculations.

In the case of the gaseous tungsten(IV) ion with a d^2 configuration, the ground state is 3F and the excited states are 3P , 1G , 1D , and 1S . A quantum mechanical selection rule forbids transitions between states of different spin multiplicity and so in the case of a d^2 ion, only transitions between the 3F and 3P states need be considered. Just as the set of five d-orbitals is split by the cubic electrostatic

field of surrounding ligands to give two or more sets of lower degeneracy, so also are the degenerate ground and excited states of a d^2 configuration. Figure 13 shows how the energies of the various states, into which the free ion terms are split, depends on the strength of the interaction of the ion with its environment (51, p. 82). The designations for these states are based on group theory symmetry properties. Additional splitting will occur under lower field symmetry to an extent depending on the strength of the ligand field (60, pp. 201-205). Thus if the environment of the ion is lowered from O_h symmetry (cubic) to that of D_{4h} (tetragonal), the degeneracy of the e_g^2 and t_{2g}^2 orbitals is lifted giving rise to non-degenerate levels of symmetry:

$$e_g^2 \rightarrow a_{1g} + b_{1g}$$

$$t_{2g}^2 \rightarrow e_g + b_{2g}$$

The spectroscopic states also split as follows:

$$O_h(\text{cubic}) \rightarrow D_{4h}(\text{tetragonal})$$

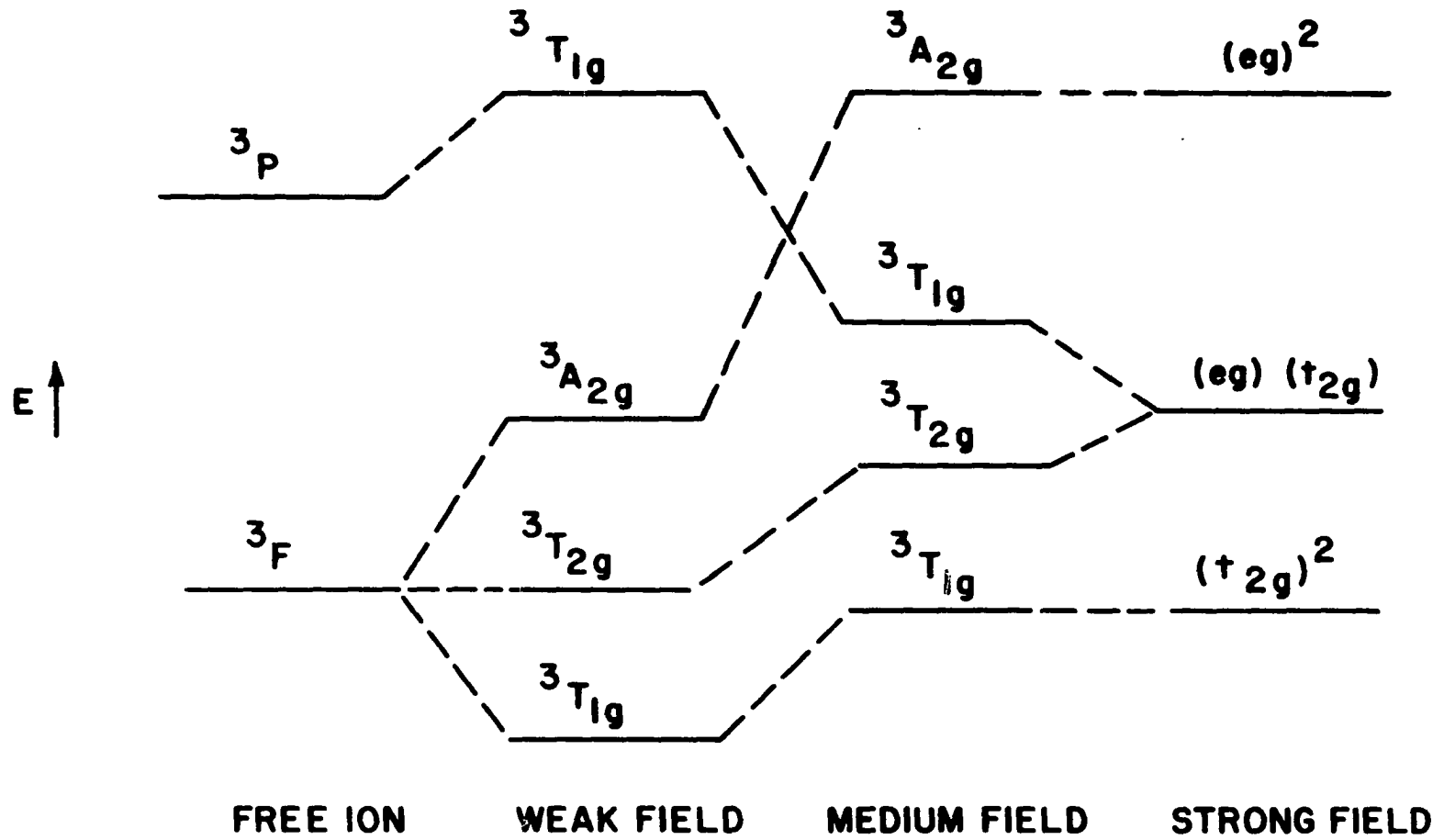
$$T_{2g} \rightarrow E_g + B_{2g}$$

$$T_{1g} \rightarrow E_g + A_{2g}$$

$$A_{2g} \rightarrow B_{1g}$$

The visible and near-ultraviolet spectra of the d^2 ions in various chemical environments result from transitions from

Figure 13. Level of splitting of d^2 in an octahedral field (not drawn to scale)



their ground state to various excited states.

The tetrahalodi(pyridine)tungsten(IV) complexes would be expected to have tetragonal symmetry and thus, in a strong field, the electronic transitions ${}^3T_{1g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g}$, ${}^3A_{2g}$, in order of increasing energy, would be expected with additional splitting of the ${}^3T_{1g}$ and ${}^3T_{2g}$ levels. The intensity of the bands occurring at wavelengths less than $330\text{m}\mu$ is sufficiently high to be in the realm of charge transfer. Thus the transition ${}^3T_{1g} \rightarrow {}^3A_{2g}$ is probably obscured by charge transfer spectra. On the other hand, splitting of the lowest level ${}^3T_{1g} \rightarrow {}^3E_g + {}^3A_{2g}$ is also not seen due to the very low energy of such a transition. The electronic transition occurring at $510\text{ m}\mu$ and $508\text{ m}\mu$ for the chloride and bromide complexes, respectively, is tentatively assigned ${}^3T_{1g} \rightarrow {}^3T_{2g}$. With the limited amount of experimental data, this is the only transition which may be assigned with any amount of certainty. The observed extinction coefficients are larger than those expected for d-d transitions by a factor of 10 - 100. A comparison of the spectra of the solids K_2WCl_6 and $\text{WCl}_4(\text{C}_5\text{H}_5\text{N})_2$ (cf. Curves 4 and 5, Figure 9) shows bands occurring in both complexes at 320 and $375\text{ m}\mu$. Charge transfer bands involving halogen in this region of the spectrum are possible. In

addition the band occurring at 550 m μ in K_2WCl_6 is not too far removed from the one at 510 m μ in $WCl_4(C_5H_5N)_2$. Thus if these bands are not due to ligand field transitions, they must be charge transfer involving halogen. It has also been suggested (35) that in complexes containing π -bonding ligands such as pyridine, electronic transitions from a bonding π -M.O., formed by overlap of the metal d_{xz} or d_{yz} atomic orbitals with the filled orbitals of the pyridine, to a non-bonding orbital, say d_{xy} on the metal, may occur. It should be kept in mind, however, that when a strong interaction between the metal ion and the ligands is present as would be expected for the tetrahalodi(pyridine)tungsten(IV) complexes, the distinction between the two types of transitions becomes clouded (57). Thus the possibility that the spectra of the pyridine complexes are caused by either or both effects cannot be ruled out at this time.

Magnetic Susceptibility of the Tetrahalodi(pyridine)-tungsten(IV) Complexes

The magnetic properties of the solid tetrahalodi(pyridine)tungsten(IV) complexes were studied to determine if the unusual diamagnetism observed for the tungsten(IV) halides was retained on complexing with pyridine. Both complexes

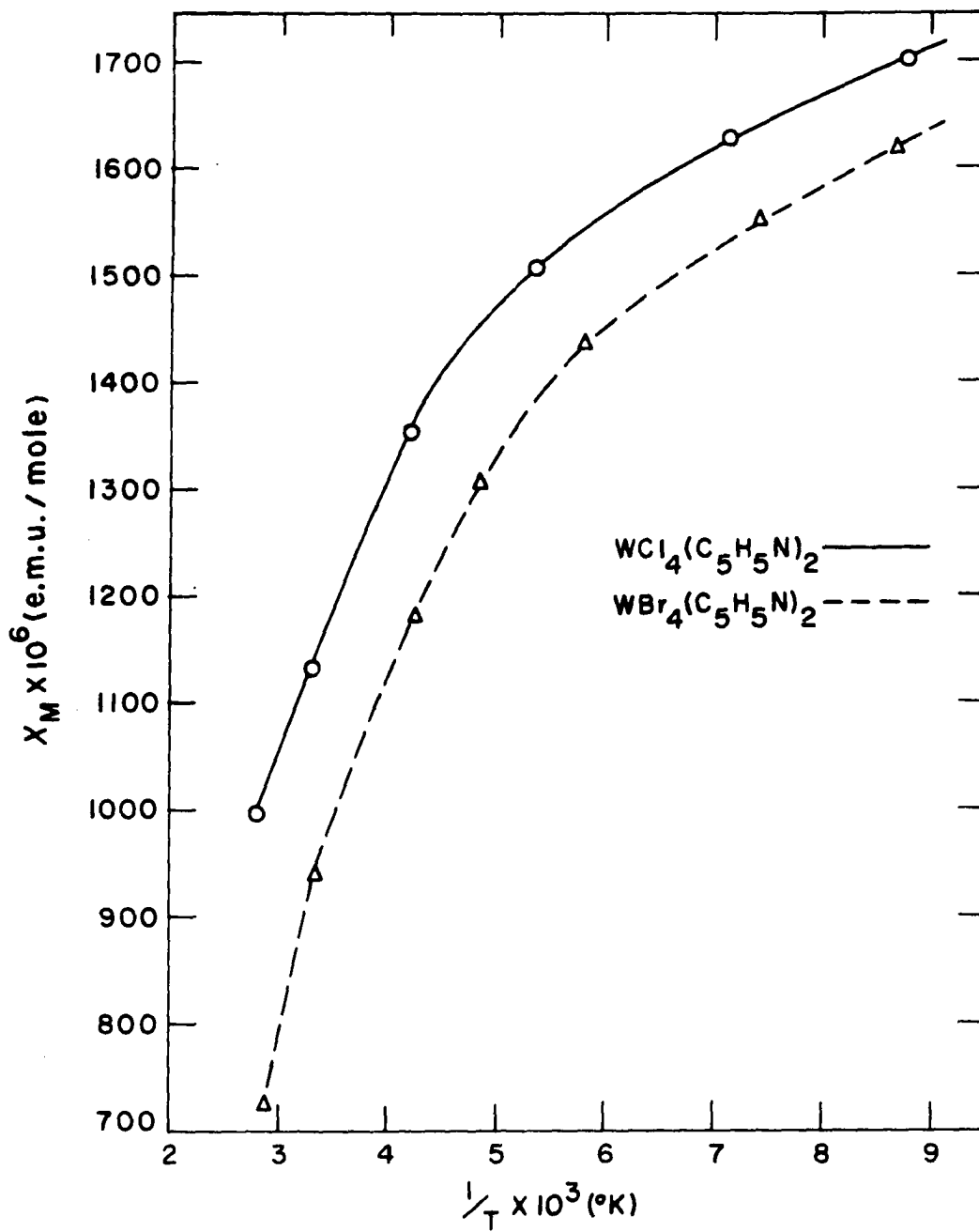
were found to be paramagnetic over the temperature range considered. This is an indication of the splitting of the metal to metal interactions (assumed to be present) in the pure tetrahalides on complexing with pyridine. The data obtained are presented in Table 13 and Figure 14. The values given for χ_M are measured susceptibilities, uncorrected for diamagnetism of the atom cores. χ_M^{corr} is the value obtained by adding the diamagnetic correction for the ligands to χ_M .

Table 13. Variation of susceptibility as a function of temperature for the tetrahalodi(pyridine)tungsten(IV) complexes

WCl ₄ (C ₅ H ₅ N) ₂			WBr ₄ (C ₅ H ₅ N) ₂		
$\chi_M \times 10^6$ (e.m.u./mole)	$\chi_M^{\text{corr}} \times 10^6$ (e.m.u./mole)	T (°K)	$\chi_M \times 10^6$ (e.m.u./mole)	$\chi_M^{\text{corr}} \times 10^6$ (e.m.u./mole)	T (°K)
998	1212	357	725	994	349
1130	1344	303	942	1211	299
1352	1566	238	1180	1449	235
1505	1719	187	1305	1574	208
1628	1842	140	1435	1704	172
1700	1914	114	1548	1817	135
			1615	1884	115

Experimentally the effective magnetic moment μ of compounds exhibiting a paramagnetic behavior is obtained from observed susceptibilities χ_M according to the Curie formula (Equation 31), or the Curie-Weiss formula (Equation 32).

Figure 14. Variation of the magnetic susceptibility of the tetrahalodi(pyridine)tungsten(IV) complexes with temperature



$$\chi_M = N\mu_{\text{eff}}^2/3kT \quad (31)$$

$$\chi_M = N\mu_{\text{eff}}/3T(T + \theta) \quad (32)$$

Where: χ_M = molar magnetic susceptibility,

T = absolute temperature,

θ = constant,

N = Avogadro's number,

μ_{eff} = effective magnetic moment,

k = Boltzmann constant.

From the Curie law it would be expected that by plotting χ_M against $1/T$, a straight line should result. The slope would be proportional to μ_{eff}^2 . If the corrections for diamagnetism and Van Vleck paramagnetism have not been made on the observed susceptibilities, an additional term, αT , which is a constant, would have to be added to Equations 29 and 30.

The limiting slope of the plot of χ_M versus $1/T$ in Figure 14 at high temperatures gives a value for μ_{eff} of 1.6 and 2.1 Bohr magnetons for $\text{WCl}_4(\text{C}_5\text{H}_5\text{N})_2$ and $\text{WBr}_4(\text{C}_5\text{H}_5\text{N})_2$, respectively, whereas a value of 2.83 Bohr magnetons would have been anticipated for two unpaired electrons with only spin angular momentum. At lower temperatures the data do not yield a straight line and it is not possible to explain the variation of the moments with temperature by a Curie-Weiss law. It is

probable that this deviation results from a population of a higher energy level over the range of temperature used for the measurements, and only at very low temperature will only the lowest level be occupied.

The fact that the observed moments are lower than that expected for two unpaired electrons arises from the high value of the spin-orbit coupling constant associated with the second- and third-row transition elements (61). The spin-orbit coupling causes additional splitting of the spectroscopic levels. This constant may be regarded as a measure of the mean energy separation between successive possible values of the total angular momentum of the ground state. Physically it indicates the 'tightness' of coupling of the spin and orbital angular momenta vectors which give rise to paramagnetism. The strength of this coupling depends upon the intensity of the electric field which the electron experiences. This field increases in intensity as it approaches the nucleus. Thus the spin-orbit coupling constant increases with: (1) the charge Z on the nucleus, and (2) the extent to which the electron approaches the nucleus. If the strength of this coupling becomes great enough, it can result in a complete destruction of the permanent magnetic moment.

Kotani (62) applied ligand field theory to the transition metal complexes and deduced the variation of the effective magnetic moment with temperature and spin-orbit interaction for d^n configurations. The theory predicts that in the case of a d^2 configuration, the moment will be markedly dependent on the temperature and the spin-orbit interaction. In deducing this relationship, Kotani assumed, (1) a perfect cubic field; (2) the effects of the ligand field to be much greater than those of the coulomb repulsion between d-electrons; (3) the coulomb repulsion to be much stronger than the spin-orbit coupling; and (4) no magnetic interaction between neighboring paramagnetic ions.

Kamimura, Koide, Sekiyama, and Sugano (63) recently showed that the Kotani theory does not apply to 4d- and 5d group ions and that the spin-orbit interaction is as important as the coulomb repulsion between the d-electrons in these ions. Thus in attempting to explain the susceptibility data of the di-pyridine adducts theoretically, the equality between the spin-orbit interaction and the coulomb repulsion between the d-electrons must be taken into account. In addition to this factor, the deviation from perfect cubic symmetry and the importance of the covalency effect in cases of 4d- and 5d

electrons must be accounted for.

Liehr and Ballhausen (64) have shown that in the strong field case, the d^2 configuration becomes the same as the d^4 with the sign of the spin-orbit coupling constant reversed. The susceptibility of a number of ruthenium(IV) and osmium(IV) compounds which have a d^4 configuration has been measured (61, 65, 66). The ruthenium(IV) and osmium(IV) compounds are examples of the strong field case as are the di-pyridine adducts of tungsten which are d^2 complexes. Thus it might be expected that the susceptibility of ruthenium(IV), osmium(IV), and tungsten(IV) compounds would show similar trends. The ruthenium(IV) compounds show an increase in paramagnetism with decreasing temperature as do the di-pyridine adducts of tungsten(IV). This temperature dependent paramagnetism is attributed to the occupation of states higher than the ground state (65).

Kennedy and Peacock (49) recently reported magnetic data for the tetrahalodi(pyridine)tungsten(IV) complexes. Their values follow the same trend as those given above although the curvature of the χ_M versus $1/T$ plots was not as great. They found a deviation from the Kotani theory and a rather large Curie temperature. They also give a Néel minimum for

$WCl_4(C_5H_5N)_2$ at $100^\circ K$. and attribute the high Curie temperatures obtained for these compounds to antiferromagnetism. Susceptibility measurements have been obtained for $WCl_4(C_5H_5N)_2$ for temperatures between liquid helium and $64^\circ K$.¹ Extrapolation of the data between this temperature region and the one given in Table 10 did not indicate the presence of a Néel point. Thus a Néel point probably does not occur in this compound and their statement concerning antiferromagnetism is not valid. Until the structure of these compounds and the theory utilizing the additional conditions mentioned above is worked out, not much more can be said about this unusual magnetic behavior.

¹Gerstein, B. C. and Jelinek, F. S., Iowa State University, Ames, Iowa. On the magnetic susceptibility of $WCl_4(C_5H_5N)_2$. Unpublished work. 1963.

SUMMARY

Solution studies of the tetrahalodi(pyridine)tungsten(IV) complexes in pyridine by conductance and absorption spectra techniques indicated the existence of two species, probably the cis or trans isomer along with the ion, $(W(C_5H_5N)_3Cl_3)^+$, in solution. From steric considerations, the complexes are probably octahedral with the molecule tetragonally distorted from true octahedral symmetry.

The magnetic susceptibility of the tetrahalodi(pyridine)-tungsten(IV) complexes yielded moments below the "spin only" value of 2.83 Bohr magnetons. Due to the asymmetry of the ligand field and large spin-orbit coupling constant, deviation from the Kotani theory is expected. Kennedy and Peacock (49) postulate the possible presence of antiferromagnetic interaction between neighboring halogen atoms to account for this unusual magnetic behavior. As indicated, however, the possibility of these compounds being antiferromagnetic is doubtful.

SUGGESTIONS FOR FUTURE WORK

The work performed in this section represents only a small part of that which might be done in connection with the study of coordination compounds of tungsten(IV) halides. At the present time there is a considerable lack of information about complexes of tungsten with organic ligands.

Before complete assignment of the electronic transitions can be made concerning the tetrahalodi(pyridine)tungsten(IV) complexes, the structure of these compounds must be worked out. Kennedy and Peacock (49) report the formation of crystalline products using the reaction between the potassium hexahalotungstates and pyridine. Complete structural analysis might be possible if good single crystals can be obtained. Also the spectra of the crystals using polarized light would further help in identifying the electronic transitions.

The preparation of other complexes and a study of their spectral and magnetic properties would be of value. Preliminary research has indicated that the tungsten(IV) halides coordinate with N,N,N',N'-tetramethylethylenediamine, trimethylamine, and triethylamine. It is further supposed that other alkyl derivatives of pyridine such as 3-picoline, 2,6-lutidine, etc. would yield derivatives. It would be helpful

if one or more of these adducts were sufficiently soluble in organic solvents such that molecular weight and dipole moments could be obtained. These measurements would further help to establish the structure of these compounds.

Additional work on the identification of the species present in the pyridine solution should be carried out. Separation and identification of the intermediate and final products would help establish the mechanism of the reaction which takes place.

During the preparation of the tetrabromodi(pyridine)tungsten(IV) complex, a small amount of a red material was obtained. This red form was extracted from the green form with pyridine. A sufficient amount of the material could not be isolated for analysis. X-ray data indicated the possible presence of an amorphous substance. The solution of this compound in pyridine was stable for at least three days. The spectrum contained a band at 522 $m\mu$ with a molar extinction coefficient of ca. 3000 $l \text{ mole}^{-1} \text{ cm.}^{-1}$. This band is in the vicinity of the one obtained for the tetrabromodi(pyridine)tungsten(IV) complex in pyridine (cf. Curve 4, Figure 10). Identification of this compound would be of value as it is possible that this material is one of the species obtained during solution of the tetrabromodi(pyridine)tungsten(IV) complex in pyridine.

BIBLIOGRAPHY

1. Scheele, C. W. Svenska Vet. Akad. Handl. 2, 89 (1781).
2. Vincent, M. F., Reed, H. W. B. and Smith, P. Polymerizations of olefins. British Patent 785,314. Oct. 23, 1957. Abstracted in Chemical Abstracts 52: 5038c. 1958.
3. Ross, W. E., McAllister, S. H. and Anderson, J. Catalyst for alkylation process. U. S. Patent 2,389,550. Nov. 20, 1957. Abstracted in Chemical Abstracts 40: 1652³. 1946.
4. Muetterties, E. L. Fluorocarbons. U. S. Patent 2,709,184. May 24, 1955. Abstracted in Chemical Abstracts 50: 6498f. 1956.
5. Konrad, F. Vinyl and vinylidene chlorides by dehydrochlorination. U. S. Patent 2,765,351. Oct. 2, 1956. Abstracted in Chemical Abstracts 51: 7399e. 1957.
6. Kashtanov, L. I. J. Gen. Chem. (U.S.S.R.) 3 229 (1933).
7. Voigt, V. A. and Blitz, W. Z. anorg. allgem. Chem. 133, 277 (1924).
8. Biltz, V. W. and Fendius, C. Z. anorg. allgem. Chem. 172, 385 (1928).
9. Blomstrand, C. W. J. prakt. Chem. 82, 430 (1861).
10. _____ J. prakt. Chem. 89, 230 (1863).
11. Hönigschmid, V. O. and Menn, W. Z. anorg. allgem. Chem. 229, 49 (1936).
12. Michael, A. and Murphy, A. Am. Chem. J. 44, 365 (1910).
13. Defacqz, M. E. Ann. chim. et phys. [7] 222, 49 (1901).
14. _____ Compt. rend. 128, 1233 (1899).
15. Teclu, N. Liebigs Ann. Chem. 187, 255 (1877).

16. Ketelaar, J. A. A., Oosterhout, G. W. and Braun, P. B. *Rec. trav. Chim.* 62, 597 (1943).
17. Ewens, R. V. G. and Lister, M. W. *Trans. Faraday Soc.* 34, 1358 (1938).
18. Ketelaar, J. A. A. and Oosterhout, G. W. *Rec. trav. Chim.* 62, 197 (1943).
19. Schaffer, H. A. and Smith, E. F. *J. Am. Chem. Soc.* 18, 1098 (1896).
20. Shchukarev, A. A., Novikov, G. I. and Kokovin, G. A. *Russian Journal of Inorganic Chemistry* 4, 995 (1959).
21. Roscoe, H. E. *Liebigs Ann. Chem.* 162, 349 (1872).
22. Riche, M. A. *Ann. chim. et phys.* [3] 50, 24 (1857).
23. Borch, J. B. J. *prakt. Chem.* 54, 254 (1851).
24. Novikov, G. I., Andreeva, N. V. and Polyachenok, O. G. *Russian Journal of Inorganic Chemistry* 6, 1019 (1961).
25. Knecht, E. and Hilbert, E. *Z. angew. Chem.* 24, 174 (1911).
26. McCarley, R. E. and Brown, T. M. *J. Am. Chem. Soc.* 84, 3216 (1962).
27. Emeleus, H. J. and Gutmann, V. *J. Chem. Soc.* 1950, 2116 (1950).
28. Brewer, L., Bromley, L. A., Gilles, P. W. and Lofgren, N. L. The thermodynamic properties of molybdenum and tungsten halides and the use of these metals as refractories. In Quill, L., ed. *The chemistry and metallurgy of miscellaneous materials.* pp. 294-297. New York, New York, McGraw-Hill Book Co., Inc. 1950.
29. Brosset, C. *Nature* 135, 874 (1935).
30. Pauling, L. *Chem. Eng. News* 25, 2970 (1947).

31. Olsson, O. Ber. 46, 566 (1913).
32. Young, R. C. J. Am. Chem. Soc. 54, 4515 (1932).
33. Hill, J. B. J. Am. Chem. Soc. 38, 2383 (1916).
34. Lindner, K. and Köhler, A. Ber. 55, 1461 (1922).
35. McCarley, R. E. and Torp, B. A. Inorg. Chem. 2, 540 (1963).
36. McCarley, R. E. and Boatman, J. C. Inorg. Chem. 2, 547 (1963).
37. Jonassen, H. B., Cantor, S. and Tarsey, A. R. J. Am. Chem. Soc. 78, 271 (1956).
38. Spitzer, L. Ind. and Eng. Chem., Anal. Ed. 8, 465 (1936).
39. National Bureau of Standards. Tables for conversion of x-ray diffraction angles to interplanar spacings. Washington, D. C., U. S. Government Printing Office. 1950.
40. Schäfer, H. and Grau, L. Z. anorg. allgem. Chem. 275, 198 (1954).
41. Dahl, L. F. and Wampler, D. L. J. Am. Chem. Soc. 81, 3150 (1959).
42. Klemm, W. and Steinberg, H. Z. anorg. allgem. Chem. 227, 193 (1936).
43. Brosset, C. Arkiv. Kem. Min. Geol. [7] 20A (1945).
44. _____ Arkiv. Kem. Min. Geol. [11] 22A (1946).
45. Powell, H. M. Ann. Rep. Prog. Chem. Soc. 43, 95 (1946).
46. McCarley, R. E., Hughes, B. G., Boatman, J. C. and Torp, B. A. Reactions of some niobium(V) and tantalum(V) halides with pyridine. In Reactions of coordinated ligands and homogeneous catalysis. Advances in Chemistry Series, No. 37. pp. 243-255. Washington, D. C., American Chemical Society. 1963.

47. Prasad, S. and Krishnaiah, K. S. R. J. Indian Chem. Soc. 38, 182 (1961).
48. Cooper, A. J. and Wardlow, W. J. Chem. Soc. 1932, 635 (1932).
49. Kennedy, C. D. and Peacock, R. D. J. Chem. Soc. 1963, 3392 (1963).
50. Burstall, F. H. J. Chem. Soc. 1936, 173 (1936).
51. Ballhausen, C. J. Introduction to ligand field theory. New York, New York, McGraw-Hill Book Co., Inc. 1962.
52. Dunn, T. M. The visible and ultra-violet spectra of complex compounds. In Lewis, J. and Wilkins, R. G. eds. Modern coordination chemistry. pp. 229-300. New York, New York, Interscience Publishers, Inc. 1960.
53. Norwitz, G. Anal. Chem. [9] 33, 1253 (1961).
54. Audrieth, L. F. and Kleinberg, J. Non-aqueous solvents. New York, New York, John Wiley and Sons, Inc. 1953.
55. Basolo, F. and Pearson, R. G. Mechanisms of inorganic reactions. New York, New York, John Wiley and Sons, Inc. 1958.
56. Wilkins, R. G. and Williams, M. J. G. The isomerization of complex compounds. In Lewis, J. and Wilkins, R. G., eds. Modern coordination chemistry. pp. 174-228. New York, New York, Interscience Publishers, Inc. 1960.
57. Orgel, L. E. J. Chem. Phys. 23, 1004 (1955).
58. Jørgensen, C. K. Absorption spectra and chemical bonding in complexes. Reading, Massachusetts, Addison-Wesley Publishing Co., Inc. 1962.
59. Bethe, H. Ann. Physik [5] 3, 133 (1929).
60. Cotton, F. A. Chemical applications of group theory. New York, New York, Interscience Publishers. 1963.

61. Ernshaw, A., Figgis, B. N., Lewis, J. and Nyholm, R. S. J. Chem. Soc. 1961, 3132 (1961).
62. Kotani, M. J. Phys. Soc. Japan 4, 293 (1949).
63. Kamimura, H., Koide, S., Sekiyama, H. and Sugano, S. J. Phys. Soc. Japan 15, 1264 (1960).
64. Liehr, A. D. and Ballhausen, C. J. Ann. Phys. (N. Y.) 2, 134 (1959).
65. Johannesen, R. B. and Candela, G. A. Inorg. Chem. 2, 67 (1963).
66. Figgis, B. N., Lewis, J., Nyholm, R. S. and Peacock, R. D. Disc. Faraday Soc. 26, 103 and 175 (1959).

ACKNOWLEDGEMENTS

The author expresses his sincere appreciation to Dr. R. E. McCarley who guided the research of the work reported herein.

Acknowledgement is made to members of Metallurgy Group VI for their generous exchange of equipment and ideas, and their useful comments and criticisms. Special thanks goes to Mr. J. C. Boatman and Mr. B. G. Hughes who proofread this dissertation.