to the cooled reaction mixture and the yellow crystalline solid was collected by filtration. After thorough washing with ethanol and pentane the solid was dried under vacuum affording 1.30 g. of product, which is insoluble in nearly all common solvents and only slightly soluble in pyridine and nitromethane. It begins to decompose above 300° but no melting point was observed up to 350°.

Anal. Calcd. for $C_7H_{13}MoN_3O_3$: C, 29.69; H, 4.63; N, 14.84. Found: C, 29.9; H, 4.75; N, 14.7.

Pyridine Complexes.—$Cr(py)(CO)_5$ and $W(py)(CO)_5$ were prepared by refluxing a mixture of the hexacarbonyl with pyridine until approximately one equivalent of CO had been evolved. The separation and purification procedures were those reported by Strohmeier and Gerlach.[12] $Mo(py)(CO_5)$ was also prepared by direct reaction, but was recrystallized from hexane at −80°. The preparation of this compound does not seem to have been reported previously.

Anal. Calcd. for $C_{10}H_5MoNO_5$: C, 38.12; H, 1.60. Found: C, 38.3; H, 1.78.

Strohmeier has reported photochemical reaction of $W(CO)_6$ with pyridine to give $W(py)_2(CO)_4$. We have prepared this and its Cr and Mo analogs by direct thermal reaction. A mixture of the metal carbonyl (1 g.) with 2.5 ml. of pyridine was refluxed until nearly two equivalents of carbon monoxide were evolved. The deeply colored mixtures were allowed to cool, whereupon an orange-yellow solid separated in each case. Pentane was added and the mixture was stirred and then filtered. The solid was washed well with pentane to remove pyridine metal pentacarbonyl and any residual carbonyl. Recrystallization was effected by dissolution in acetone followed by precipitation by addition of water. The bis-(pyridine) chromium tetracarbonyl complex is very unstable and decomposes readily in air to form pyridine chromium pentacarbonyl (as shown by infrared), free pyridine (odor), and a green solid insoluble in organic media, which may be Cr_2O_3. Yields, analyses, etc., are given in Table V for the Cr and Mo compounds, both of which are yellow-orange in color. The properties of the W compound were as previously reported.[12]

α,α-Dipyridyl Complexes.—These were all prepared by the method used by Abel, Bennett, and Wilkinson[5] for α,α-dipyridyl molybdenum tetracarbonyl.

Spectral Measurements.—The infrared spectra in the CO stretching region all were obtained with a Baird spectrophotometer equipped with a lithium fluoride prism. Polystyrene film was used to provide calibration bands which were placed on each spectrum as it was recorded.

---

[12] W. Strohmeier and K. Gerlach, *Z. Naturforsch.*, **15b**, 413, 621 (1961).

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

The Preparation and Properties of Niobium(IV) Compounds. I. Some Niobium(IV) Halides and their Pyridine Adducts[1a]

BY ROBERT E. McCARLEY AND BRUCE A. TORP[1b]

Received September 8, 1962

Reaction of $NbBr_5$ and niobium metal in a sealed tube under a temperature gradient from 410 to 350° gave $NbBr_4$ in good yields. However, an increase in the higher temperature from 410 to 450° was sufficient to eliminate $NbBr_4$ as a product and cause deposition of a lower bromide. The halides $NbCl_4$ and $NbBr_4$ are isomorphous solids of orthorhombic structure and lattice constants $a = 8.12$, $b = 8.88$, $c = 6.84$ Å. and $a = 8.60$, $b = 9.31$, $c = 7.19$ Å., respectively; both solids are diamagnetic over the range −196 to 25°. Formation of the tetrahalodi-(pyridine)-niobium(IV) complexes resulted from the reactions of the pure tetrahalides (Cl, Br, I) with pyridine at room temperature; at elevated temperatures a second form of $NbBr_4(py)_2$ crystallized from pyridine. Evidence bearing on the structure of the pyridine adducts was obtained from conductance, spectral, and magnetic susceptibility measurements. The complexes are paramagnetic and exhibit moments much lower than the spin-only value for one magnetic electron; the spectra of solutions in pyridine show intense bands in the visible region which have been attributed to charge transfer transitions.

Introduction

In contrast to the abundance of literature pertaining to the chemistry and compounds of niobium(V) is the relatively small volume of information which describes and elucidates the chemistry of niobium in its lower oxidation states. In particular, the coördination and solution chemistry of lower valent niobium has suffered most. The latter situation is in large measure a result of the rather limited conditions under which stable solutions of niobium(V) can be obtained in aqueous media. Consequently aqueous solutions of niobium(V) have not served as a particularly fruitful starting point for the preparation of compounds or solutions of the element in the lower oxidation states. Furthermore where the lower valence states have been obtained under these conditions they are characterized by low stability and high reactivity.[2]

In view of the foregoing facts and the great affinity of the highly acidic niobium(V) compounds for oxide it seemed prudent to eliminate the troublesome water (more generally hydroxylic and other oxygenated solvents, and solvents containing acidic hydrogen) and to consider reactions in basic, but (for our purposes) innocuous solvents such as tertiary amines, nitriles, etc. Indeed, it was found that solutions of the niobium(V) halides (chloride, bromide, and iodide) in pyridine actually were reduced by the solvent producing in each instance the dipyridine adduct of the niobium(IV)

---

(1) (a) Contribution No. 1224. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) This paper is taken in part from the thesis by B. A. Torp to the Iowa State University in partial fulfillment of the requirements for the degree of Master of Science.

(2) V. Cozzi and S. Vivarelli, *Z. anorg. allgem. Chem.*, **279**, 165 (1955).

(3) R. E. McCarley, B. G. Hughes, J. C. Boatman, and B. A. Torp, in "Reactions of Coordinated Ligands and Homogeneous Catalysis," Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, pp. 243–255.

halide.[3] It is the purpose of this paper to describe more fully the preparation and properties of these interesting derivatives of niobium(IV).

For preparation of the pyridine adducts, the pure niobium(IV) halides were chosen as starting materials since the reduction by pyridine of the niobium(V) halides yielded mixtures which were difficult to free entirely of the pyridine oxidation products. Whereas the preparations of $NbCl_4$[4,5] and NbI_4[6] have been investigated extensively, only recently has a synthesis of $NbBr_4$ been reported.[7] A useful synthesis of both $NbCl_4$ and $NbBr_4$ is described herein.

Experimental

Since the niobium(IV) halides and their pyridine derivatives are extremely sensitive to moisture and air, all materials used in the preparations were rigorously dried and stored in evacuated vessels. Whenever this was not possible, as in the case of solid or gaseous materials, these were purified immediately before use. In all preparations and experiments with these niobium compounds, sealed and evacuated glass vessels were used. Storage and handling of these materials was done in a drybox under an argon atmosphere or on a vacuum line. The drybox was maintained at a dew point of *ca.* −75° by circulation of the atmosphere through a column of Molecular Sieves (Linde).

Materials.—Niobium metal was prepared by reduction with carbon of high purity niobium pentoxide[8] obtained from the Fansteel Metallurgical Corporation. The resulting metal was either purified by the crystalbar process,[9] or by vacuum sintering at high temperatures to reduce the oxygen content to an acceptable level (less than 200 p.p.m.). Chlorine gas, in a lecture size cylinder from the Matheson Co., was purified just before use by condensing the gas in a vessel immersed in a Dry Ice–acetone bath. The liquid chlorine was outgassed on the vacuum line at −196° before a reaction was begun. Bromine was first dried over outgassed phosphorus(V) oxide. This material was then distilled, *in vacuo*, into a flask fitted with a vacuum stopcock for storage. Bromine purified in this manner was used in several experiments by distillation of a portion of the liquid from the storage vessel into the desired reaction tube. Iodine was purified by outgassing at 10^{-6} mm. or by sublimation, *in vacuo*, at *ca.* 80° just before its use in a reaction.

The pyridine used in this work was a spectro-grade reagent obtained from the Eastman Co. The liquid was dried by a series of successive distillations, *in vacuo*, from barium oxide and calcium hydride. The pyridine was refluxed for several days over the drying agents and finally vacuum distilled into a flask for storage. Solvent dried in this manner had a specific conductance of less than 10^{-7} ohm^{-1} cm.$^{-1}$ at 25°.

Analytical Methods.—The niobium content of all niobium(IV) halides and pyridine complexes was determined gravimetrically by ignition of the compound to Nb_2O_5. In order to determine the amount of niobium(IV) in a sample and to check the ignition method, an oxidimetric method also was utilized. The sample was oxidized to niobium(V) with an excess of acidic iron(III) sulfate solution in an inert atmosphere. The iron(II) formed subsequently was titrated with standard cerium(IV) sulfate solution using ferroin indicator.

The halide content in a sample was determined by the standard Volhard method. The compound was hydrolyzed with dilute aqueous ammonia, hydrated niobium oxide was removed by filtration, and the usual analytical procedure was followed in subsequent steps.

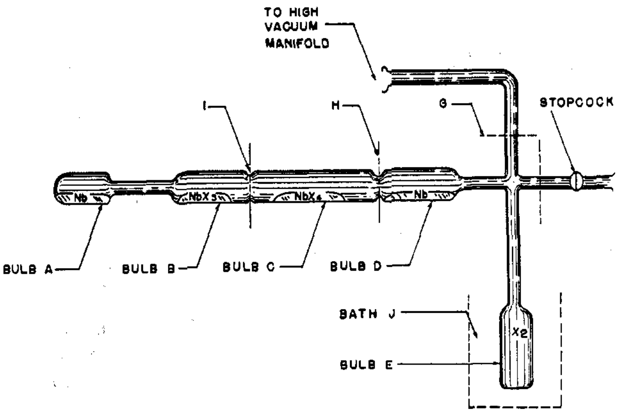

Fig. 1.—Apparatus for the preparation of $NbCl_4$ and $NbBr_4$.

Pyridine in the niobium complexes was determined by two methods. The approximate pyridine content of the compounds was determined from weight gain data. More accurate values were obtained by hydrolyzing a complex in concentrated sodium hydroxide solution and distilling the liberated pyridine into glacial acetic acid. The pyridine content subsequently was determined in glacial acetic acid by titration with standard perchloric acid in the same solvent, using methyl violet as an indicator.[10]

Preparation of Niobium(IV) Chloride and Niobium(IV) Bromide.—The preparations of $NbCl_4$ and $NbBr_4$ were accomplished by the reduction of the appropriate niobium(V) halide with niobium metal as described by Schäfer and Dohmann.[4,7] Their apparatus was modified to permit both the preparation of niobium(V) halide and its reduction to be accomplished in one reaction vessel (Fig. 1).

In the preparation of $NbCl_4$, niobium metal turnings (5–10 g.) were first placed in a Pyrex reaction tube at points A and D and the apparatus outgassed at 10^{-6} mm. A chlorine cylinder then was connected to stopcock F and 10–20 ml. of liquid condensed in bulb E, which was cooled in a Dry Ice–acetone bath (J). After outgassing the liquid chlorine, the vessel was sealed off from the system at points G and ahead of stopcock F.

Niobium(V) chloride first was prepared by placing bulb A in a resistance furnace which was maintained at 350°. The vapor pressure of chlorine in the system was kept at *ca.* 70 mm. with a Dry Ice–acetone bath (J) around bulb E. Under these conditions chlorine gas reacted with hot niobium to form volatile $NbCl_5$ which deposited in bulb B as bright yellow needles.

After 10–20 g. of $NbCl_5$ had formed, the used-metal bulb (A) and the chlorine bulb (E) were sealed off. The resulting straight tube was placed in a temperature gradient from 400° (Nb end) to 250° ($NbCl_5$ end) maintained in a metal-lined double furnace. After several days under these conditions, brownish purple crystals of $NbCl_4$ (5–10 g.) collected in bulb C of the reaction vessel. The used metal bulb (D) then was sealed off at H and the product tube taken into the drybox and broken at point I. Pure $NbCl_4$ was easily removed from bulb C and stored in the argon atmosphere until needed.

Anal. Calcd. for $NbCl_4$: Nb, 39.6; Cl, 60.4. Found: Nb, 39.7; Cl, 60.3.

The synthesis of $NbBr_4$ was accomplished in much the same manner as described for $NbCl_4$. The apparatus was very similar to Fig. 1, except stopcock F was omitted. After loading the reaction vessel, 10–20 ml. of dry bromine was distilled into bulb E, which was immersed in an ice bath (J). The liquid bromine was outgassed and the apparatus sealed off from the system.

Niobium(V) bromide subsequently was prepared by reaction

---

(4) H. Schäfer and K. D. Dohmann, *Z. anorg. allgem. Chem.*, **299**, 197 (1959).

(5) H. Schäfer, C. Göser, and L. Bayer, *ibid.*, **265**, 258 (1951).

(6) J. D. Corbett and P. W. Seabaugh, *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).

(7) H. Schäfer and K. D. Dohmann, *Z. anorg. allgem. Chem.*, **311**, 134 (1961).

(8) H. A. Wilhelm and E. R. Stevens, U. S. Atomic Energy Commission Report IS-339, Feb., 1961.

(9) R. F. Rolsten, *J. Electrochem. Soc.*, **106**, 975 (1959); *Trans. Met. Soc. AIME*, **215**, 478 (1959).

(10) J. A. Fritz, *Anal. Chem.*, **25**, 410 (1953).

of bromine vapor with niobium metal at 400–450° for several days at a bromine pressure in the system of *ca.* 210 mm. The $NbBr_5$ deposited in bulb B as bluish purple crystals which were visibly contaminated only with traces of yellow $NbOBr_3$.

After sealing off the used portions of the apparatus, $NbBr_4$ was prepared by the reduction of $NbBr_5$ according to the reaction

$$4NbBr_5(g) + Nb(s) = 5NbBr_4(g) \qquad (1)$$

This was accomplished by placing the reaction tube in a temperature gradient from 350° ($NbBr_5$ end) to 410° (Nb end), the gaseous $NbBr_4$ crystallizing in bulb C as reddish blue crystals. The product (5–10 g.) was removed in a pure form according to the procedure given for $NbCl_4$. Excess $NbBr_5$, $NbOBr_3$, and lower niobium bromides did not interfere with the preparation as they were either more or less volatile than $NbBr_4$ and remained in bulbs B or D.

Anal. Calcd. for $NbBr_4$: Nb, 22.5; Br, 77.5. Found: Nb, 22.6; Br, 77.4.

Preparation of Niobium(IV) Iodide.—NbI_4 was prepared by the thermal decomposition of NbI_5 as described by Corbett and Seabaugh.[6]

Anal. Calcd. for NbI_4: Nb, 15.5; I, 84.5. Found: Nb, 15.4, 15.6; I, 84.1, 84.5.

Preparation of Niobium(IV) Halide Complexes by Reaction with Pyridine at Room Temperature.—All preparations of niobium(IV) halide complexes were accomplished by the direct reaction of the appropriate tetrahalide with excess pyridine. The reactions were performed in round-bottom vessels provided with a magnetic stirring bar, stopcock, and ball joint for attachment to the vacuum line.

In a typical experiment, 2–3 g. of NbX_4 (X = Cl, Br, I) were transferred, in the drybox, to a reaction vessel and outgassed on the vacuum line. Pyridine (50 ml.) then was vacuum distilled into the vessel at 0°, warmed to room temperature, and the complexing reaction was allowed to proceed with stirring. In each case the solution became more intensely colored as the reaction progressed. When saturation of the solution was achieved, the solid complex precipitated in a microcrystalline state. After the complexing reaction had been completed, excess pyridine was removed by vacuum distillation and the solid product dried to constant weight under high vacuum.

A complexing reaction was judged to be complete by noting the disappearance of unreacted tetrahalide in the reaction vessel. This observation later was confirmed by X-ray diffraction patterns of the solid complexes which showed no lines attributable to unreacted NbX_4.

Tetraiododi-(pyridine)-niobium(IV).—In the reaction of NbI_4 with pyridine, the solution immediately turned a bright green color. As the complexing reaction progressed, this color deepened until after several hours the solution appeared deep purple and dark crystals were visible in the flask. In 24 hr. the NbI_4 had disappeared and excess pyridine was removed, leaving a deep purple solid. This solid was very hard and glassy and was extremely difficult to dry to a constant weight. During several days of pumping under high vacuum at room temperature, the solid residue gradually lost weight until a constant py/NbI_4 ratio of 2.2 (calculated from weight gain data) was reached. Further vacuum treatment at 50° did not decompose the complex and reduced this ratio to 2.1. The $NbI_4(py)_2$ complex was dark brown when finely powdered and hydrolyzed slowly in air, but was stable indefinitely when kept in an inert atmosphere.

Anal. Calcd. for $NbI_4(py)_2$: Nb, 12.2; I, 66.9; py, 20.9. Found: Nb, 11.9; I, 65.2; py, 20.8.

Tetrabromodi-(pyridine)-niobium(IV).—In contrast with the preparation of $NbI_4(py)_2$ described above, the reaction of $NbBr_4$ with pyridine took place much more slowly. The reaction mixture gradually turned a light orange color until after several hours a green solid began to precipitate. The complexing reaction was completed in 2 to 3 days with a large volume of solid product present in the flask. After removing the excess solvent, this solid was powdery and bright green, while a slight amount of a red product deposited on the walls of the flask. This red solid was later isolated by high temperature extraction and found to have the same composition as the green product. The solid green residue readily attained a constant py/$NbBr_4$ ratio of *ca.* 1.9 (from weight gain data) at room temperature. The compound was stable in the absence of air and moisture.

Table I

Interplanar Spacings for Some Tetrahalodi-(pyridine)-niobium(IV) Complexes

$NbCl_4(py)_2$ *d*, Å.^{a}	$NbBr_4(py)_2$ (green) *d*, Å.^{a}	$NbBr_4(py)_2$ (red) *d*, Å.^{a}	$NbI_4(py)_2$ *d*, Å.^{a}
8.20 (3)	6.62 (10)	9.02 (10)	6.76 (10)
6.50 (10)	6.27 (5)	8.12 (7)	5.58 (3)
6.12 (10)	5.30 (6)	6.59^b(9)	4.35 (3)
5.76 (1)	4.21 (4)	5.34^b(5)	4.07 (3)
5.37 (3)	4.04 (2)	4.70 (1)	3.94 (10)
5.16 (9)	3.88 (9)	4.48 (1)	3.85 (10)
4.15 (7)	3.69 (7)	4.09 (4)	3.47 (10)
3.83 (10)	3.27 (8)	3.98 (5)	3.31 (5)
3.71 (5)	3.14 (4)	3.88^b(4)	2.79 (10)
3.16 (8)	2.85 (1)	3.72 (1)	2.57 (8)
2.81 (5)	2.78 (3)	3.60 (10)	2.26 (2)
2.69 (4)	2.71 (4)	3.29^b(2)	2.20 (2)
2.58 (9)	2.64 (9)	3.20 (4)	2.15 (6)
2.50 (9)	2.53 (7)	3.05 (1)	2.03 (4)
2.44 (3)	2.49 (2)	2.66^b(6)	1.98 (6)
2.36 (5)	2.42 (6)	2.54^b(4)	1.84 (3)
2.33 (5)	2.13 (1)	2.49 (4)	1.80 (3)
2.10 (5)	2.09 (1)	2.44 (1)	1.74 (1)
2.03 (4)	2.05 (6)	2.30 (4)	1.67 (1)
2.00 (4)	2.02 (4)	2.23 (3)	1.56 (3)
1.97 (4)	1.94 (3)	2.16 (1)	1.40 (2)
1.92 (3)	1.90 (6)	2.11 (1)	1.36 (2)
1.87 (6)	1.82 (2)	2.06 (2)	
1.84 (6)	1.75 (4)	2.02 (2)	
1.77 (3)	1.73 (2)	1.91 (4)	
1.70 (3)	1.70 (3)	1.87 (4)	
1.66 (3)	1.54 (1)		
1.52 (4)	1.52 (5)		
1.48 (6)			

[a] All intensities were estimated visually relative to a value of 10 for the most intense line; the intensity values are given in parentheses. [b] Spacings which correspond to the most intense lines in the pattern of green $NbBr_4(py)_2$.

Anal. Calcd. for $NbBr_4(py)_2$: Nb, 16.3; Br, 56.0; py, 27.7. Found: Nb, 16.6; Br, 56.0; py, 27.9.

Tetrachlorodi-(pyridine)-niobium(IV).—The reaction of $NbCl_4$ with pyridine proceeded in a manner similar to the $NbBr_4$ reaction. The reaction mixture turned a deepening shade of red with a red-brown solid precipitating after several hours. After the reaction had been completed, the excess pyridine was removed, leaving a powdery red-brown residue that rapidly attained a constant py/$NbCl_4$ ratio of 2.0 (from weight gain data). As with the other pyridine complexes, this product was stable only under an inert atmosphere. X-Ray diffraction data for this compound and the pyridine complexes described above are given in Table I.

Anal. Calcd. for $NbCl_4(py)_2$: Nb, 23.6; Cl, 36.1; py, 40.3. Found: Nb, 23.9; Cl, 36.0; py, 38.0.

Preparation of Niobium(IV) Halide Complexes by Extraction with Pyridine at 60°.—In order to determine if any different forms of the tetrahalodi-(pyridine)-niobium(IV) complexes could be prepared by reaction at temperatures above room temperature, the tetrahalides were extracted with pyridine at 60°. The apparatus was essentially a Soxhlet extractor with the appropriate tetrahalide placed on the fritted disk and pyridine distilled into the vessel below. The pyridine was maintained at 80° in an oil bath with the condensing portion of the extractor at 60° in a hot air bath created by a heat lamp. This temperature gradient allowed the pyridine to condense above the frit at a temperature high enough to create efficient extraction of the tetrahalide. After the extraction had been completed (several days), excess pyridine was removed by vacuum distillation and the solid residue dried under high vacuum.

The extraction of $NbCl_4$ with pyridine yielded a product identical in all respects with that obtained from the reaction at room temperature. However a somewhat different, but inconclusive result was obtained from the experiment on the high temperature extraction of NbI_4. Upon removing solvent pyridine from the extracted solution, a gummy solid was obtained; further work with this material was very difficult since it was not possible to entirely remove solvent pyridine. Several days on the vacuum line lowered the pyridine:niobium ratio to only 3.7, and further work with the material was not attempted.

Red Tetrabromodi-(pyridine)-niobium(IV).—When $NbBr_4$ was extracted with pyridine at 60°, a red solid was recovered from the pyridine solution. The $NbBr_4$ first reacted with pyridine to form the usual green solid on the fritted disk. The green solid then was slowly dissolved and extracted by the hot solvent, producing an intensely red solution. As solvent in the lower vessel became saturated with solute, shiny red-brown needles began to separate from the solution. Analysis of the red crystals indicated them to be either an isomer or polymorph of the green form of $NbBr_4(py)_2$. Powdered samples of the red solid were found to change slowly to the green form on long standing. Also the X-ray diffraction pattern of the red solid always showed some lines attributable to the green form of $NbBr_4(py)_2$, as indicated in Table I.

Anal. Calcd. for $NbBr_4(py)_2$: Nb, 16.3; py, 27.7. Found: Nb, 16.5; py, 25.2.

X-Ray Diffraction Measurements.—X-Ray diffraction studies were carried out on both the niobium(IV) halides and their pyridine complexes using powder techniques. The powdered samples were contained in 0.2-mm. Lindemann capillaries that had been filled in the drybox and sealed immediately on removal. An 11.459-cm. Debye-Scherrer camera was used with Ni-filtered Cu Kα radiation. Exposure times varied between 15 and 20 hr.

Visible Spectra.—Measurements of the visible spectra of the tetrahalodi-(pyridine)-niobium(IV) complexes in pyridine were carried out in the region 300 to 700 mμ using a Cary Model 14 recording spectrophotometer. The apparatus used in this study (Fig. 2) was constructed so that concentration changes could be made without opening the vessel and destroying the complex. This vessel consisted of a Pyrex mixing chamber sealed to a cylindrical quartz cell (1-cm. light path) through a fine porosity fritted disk. A second arm from the mixing chamber was connected to a high vacuum manifold. A complex was prepared in the mixing chamber by distilling pyridine onto several crystals of tetrahalide and sealing off the vessel from the vacuum system. By alternately filtering the colored solution and distilling pyridine between the mixing chamber and the cell, a concentration of colored species was obtained in the quartz cell that gave suitable peaks within the range of the spectrophotometer. Pure pyridine was used as a reference solvent. Molar extinction coefficients for the spectrum of a complex were calculated after analyzing a known volume of solution in the quartz cell for niobium. The concentration of niobium was determined spectrophotometrically[11] after opening the cell and removing pyridine and the halides by successive evaporations with NaOH and H_2SO_4.

Other Measurements.—Magnetic susceptibility measurements of the compounds studied were obtained from −196 to 25° using a Faraday balance. Powdered samples were contained in evacuated cylindrical Pyrex bulbs 1 cm. long and 0.5 cm. in diameter. Corrections for the diamagnetism of the Pyrex bulbs were applied in all cases.

Measurements of electrolytic conductance of pyridine solutions of the $NbX_4(py)_2$ complexes were made with a Leeds and Northrup Model 4866-60 a.c. conductance bridge. The conductance apparatus consisted of an all-glass cell connected to a mixing chamber through a fritted disk. Platinum electrodes were sealed into the cell forming a vacuum tight junction with the glass. Solutions to be measured were prepared, *in vacuo*, in the mixing chamber and filtered into the cell. In this manner any atmospheric contamination was avoided.

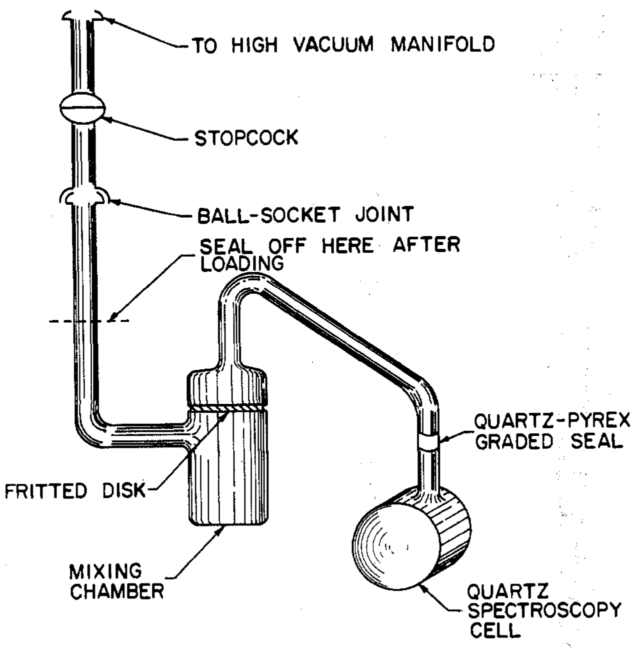

Fig. 2.—Apparatus for determination of the spectra of pyridine solutions of niobium(IV) halides.

Results and Discussion

The Niobium(IV) Halides.—The method used by Schäfer and Dohmann[7] for the preparation of $NbBr_4$ was modified to effect a faster rate of reaction and increase the yield of pure compound. It was found that the conditions necessary for the synthesis of $NbBr_4$ were bounded on one hand by low temperatures insufficient for a satisfactory reaction rate, *i.e.*, about 300° at the cool end of the tube controlling the $NbBr_5$ vapor pressure and about 350° at the hot end, which controlled the rate of the reduction reaction. On the other hand, temperatures much higher than those given in the Experimental section resulted in formation of a lower bromide phase, presumably the previously reported $NbBr_3$.[7,12] Thus changing the temperature of the niobium metal (hot end) from 410 to 450° was sufficient to produce the lower bromide rather than the desired $NbBr_4$. Therefore the disproportionation pressure of $NbBr_5(g)$ over $NbBr_4(s)$ at >410 but $<450°$ must be greater than *ca.* 600 mm., the pressure of $NbBr_5$ maintained in the reaction tube. However, within the conditions specified, good yields of highly crystalline $NbBr_4$ may be obtained.

The reported diamagnetism of all three niobium(IV) halides[5,7] was verified by our measurements over the temperature range −196 to 25°. Since Nb(IV) should otherwise be expected to possess one unpaired electron, the halides $NbCl_4$ and $NbBr_4$ most likely have metal–metal interaction in the solids, resulting in electron pairing between adjacent niobium atoms. This type of

---

(11) G. Telep and D. F. Boltz, *Anal. Chem.*, **24**, 163 (1952).

(12) C. H. Brubaker and R. C. Young, *J. Am. Chem. Soc.*, **73**, 4179 (1951).

TABLE II

CALCULATED AND OBSERVED *d*-SPACINGS FOR $NbCl_4$ AND $NbBr_4$

$NbCl_4$			$NbBr_4$		
d_{obsd},[a] Å.	d_{calcd}, Å.	*hkl*	d_{obsd},[a] Å.	d_{calcd}, Å.	*hkl*
6.02 (10)	5.99	110	6.34 (8)	6.31	110
4.45 (9)	4.44	020	4.67 (5)	4.66	020
4.09 (8)	4.06	200	4.29 (5)	4.29	200
3.43 (2)	3.42	002	3.59 (4)	3.59	002
2.95 (3)	2.96, 2.97	030, 112	3.44 (1)	3.42	211
2.71 (8)	2.71	022, 300	3.22 (4)	3.16	220
2.61 (9)	2.62, 2.59	202, 310	3.10 (8)	3.10, 3.12	030, 112
2.57 (5)	2.57	122, 131	2.96 (4)	2.92	130
2.22 (7)	2.22, 2.20	040, 103	2.84 (10)	2.84	022
2.17 (2)	2.16, 2.19	132, 321	2.76 (9)	2.76, 2.74	202, 310
2.14 (3)	2.14, 2.12	140, 302	2.71 (1)	2.70	122
2.03 (7)	2.03, 2.04	400, 141	2.40 (1)	2.40, 2.38	003, 131
1.99 (2)	1.99, 1.98	203, 410	2.33 (5)	2.33, 2.31	040, 321
1.92 (1)	1.92, 1.90	331, 411	2.29 (3)	2.31	103
1.87 (4)	1.87, 1.86	241, 042	2.25 (5)	2.25, 2.26	140, 132
1.83 (2)	1.85, 1.81	420, 142	2.15 (6)	2.15, 2.14	400, 141
1.75 (7)	1.75, 1.74	402, 303	1.98 (1)	2.01	411
1.72 (6)	1.72, 1.73	340, 150	1.96 (1)	1.95	420, 042
1.71 (2)	1.71	313, 004	1.85 (8)	1.86, 1.84	050, 303
1.64 (4)	1.64, 1.62	114, 422	1.81 (3)	1.81, 1.82	313, 150
1.61 (6)	1.62, 1.60	500, 510	1.80 (6)	1.80	004, 340
1.51 (6)	1.52, 1.50	403, 440	1.76 (1)	1.76, 1.77	104, 430
1.48 (6)	1.48	060	1.74 (3)	1.73	114
1.36 (3)	1.35	433, 015	1.70 (6)	1.71, 1.72	422, 500
1.31 (3)	1.31, 1.30	404, 334	1.64 (2)	1.64, 1.63	143, 124
1.21 (2)	1.22, 1.20	305, 460	1.59 (4)	1.60, 1.58	403, 440
1.18 (1)	1.18	504	1.55 (5)	1.55	060, 502
1.17 (1)	1.17	045	1.51 (4)	1.51, 1.52	423, 304
1.15 (2)	1.15	640	1.47 (1)	1.47, 1.46	053, 234
			1.42 (4)	1.42	433, 015
			1.38 (4)	1.38, 1.37	404, 334
			1.27 (2)	1.28, 1.29	305, 054
			1.23 (2)	1.24, 1.22	504, 045
			1.19 (2)	1.19, 1.20	405, 006

[a] Relative Intensity values are given in parentheses.

interaction has been established for α-NbI_4.[13] However, it does not appear that $NbCl_4$ and $NbBr_4$ are isomorphous with α-NbI_4.

Powder patterns of $NbCl_4$ and $NbBr_4$ were indexed on the basis of an orthorhombic unit cell containing four formula units. The lattice constants for $NbCl_4$ and $NbBr_4$ are, respectively: $a = 8.12$, $b = 8.88$, $c = 6.84$ Å., and $a = 8.60$, $b = 9.31$, $c = 7.19$ Å. For $NbBr_4$ the observed density, 4.65 ± 0.1 g. cc.$^{-1}$, was in satisfactory agreement with the calculated value of 4.77 g. cc.$^{-1}$. Although α-NbI_4 is also orthorhombic it has a larger unit cell containing eight formula units.

Further work on the structure of $NbCl_4$ and $NbBr_4$ has been hampered by difficulties in finding suitable single crystals. Small needles of either compound, thought to be single crystals by examination under the microscope, gave Weissenberg photographs which indicated the presence of highly oriented, individual filaments, or perhaps extreme twinning. It was on the basis of these photographs, however, that rough lattice parameters first were calculated to aid in the indexing of the powder patterns. A comparison of the calculated and observed *d*-spacings is given in Table II. Powder patterns of $TaCl_4$, $TaBr_4$,[14] $MoBr_4$, and WBr_4[15] also have been indexed successfully on the assumption that they are isomorphous with $NbCl_4$ and $NbBr_4$. Further structural work now in progress on thet ungsten, molybdenum, and tantalum homologs should provide a better understanding of the structure and magnetic properties of the niobium compounds.

Pyridine–Niobium(IV) Halide Complexes.—In contrast to the usually rapid and exothermic reaction of higher valent metal halides with amines, the reactions of the niobium(IV) halides proceeded very slowly at room temperature. At least partly responsible for this behavior is the rather low solubility of the resulting $NbX_4(py)_2$ complexes, and the probable polymeric structure of the niobium(IV) halides, with consequentially high lattice energies. It sometimes was observed that $NbBr_4$ and $NbCl_4$ first reacted with pyridine to produce a green and brown coating, respectively, on the surface of the tetrahalide crystals. Subsequent reaction may have been slow because of the insolubility and protective nature of the surface coating. Even at higher temperatures complete extraction of small amounts of the chloride and bromide complexes required several days; their solubilities were measured roughly to be in the millimolar range at room temperature. No other effective solvents were found for the pyridine complexes. The behavior of $NbI_4(py)_2$ was exceptional in that its solubility in pyridine was much higher than that of the chloride and bromide homologs. It also produced intensely green solutions, whereas the chloride and bromide derivatives produced red solutions.

In order to obtain more information about the structures of the pyridine complexes, the conductances and spectra of the pyridine solutions and the magnetic susceptibilities of the solids were measured. Of particular interest in this respect, also, was the elucidation of the structural difference between the green and red forms of $NbBr_4(py)_2$. Conductance measurements on solutions *ca.* 1 to 10 m*M* in either $NbCl_4(py)_2$ or $NbBr_4(py)_2$ (green form) showed no increase in conductance at room temperature over that observed for the solvent; a similar result was obtained for solutions heated at 60°. Thus it is clear that neither the chloride nor the bromide complex is appreciably ionized in solution. Since the red form of $NbBr_4(py)_2$ crystallized from pyridine at the higher temperature it also is a non-electrolyte, if indeed the green and red forms maintain their distinctive identities in solution. Data from the spectra of solutions bearing on the latter question give conflicting evidence, as discussed below.

An increase in conductance occurred on dissolving NbI_4 in pyridine, indicating slight ionization of the complex or the occurrence of some decomposition reaction. The last possibility is suggested by the spectra of the solutions of NbI_4, which exhibit an intense absorption band at 370 mμ as shown in Fig. 3. Occurrence of this peak at 370 mμ suggests the presence of triiodide ion, which also shows an intense absorption maximum at *ca.* 370 mμ in pyridine.[16] In view of the ready reduction of NbI_5 in pyridine,[3] with formation of $NbI_4(py)_2$ and iodine, it is possible that further reaction by means of an equilibrium of type 2 may take place, yielding an equilibrium concentration of iodine sufficient to

---

[13] L. F. Dahl and D. L. Wampler, *J. Am. Chem. Soc.*, **81**, 3150 (1959).

[14] R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, **2**, 547 (1963).

[15] R. E. McCarley and T. M. Brown, unpublished research.

[16] J. Kleinberg, E. Colton, J. Sattizahn, and C. A. Vander Werf, *J. Am. Chem. Soc.*, **75**, 442 (1953).

$$NbI_4(py)_2 + py = NbI_3(py)_3 + {}^1/_2I_2 \qquad (2)$$

account for the absorption at 370 mμ and the small conductance of the solution. Ionization of iodine in pyridine[17] has been postulated to proceed according to reaction 3.

$$pyI_2 + I_2 = pyI^+ + I_3^- \qquad (3)$$

A small absorption peak at *ca.* 610 mμ was found in the spectra of rather concentrated solutions of NbI_4, but a peak in this region was not observed in the spectra of $NbCl_4$ and $NbBr_4$ solutions. It is possible that the presence of this weak band also may be associated with the decomposition process and formation of the species indicated as $NbI_3(py)_3$ in (2). Although an absolute deduction of the species in the NbI_4 solutions cannot be made on the basis of this evidence, it seems certain that more than one species is present. Because of the limited solubility of $NbI_4(py)_2$ in other solvents, determinations of the spectra in solutions where competing reactions such as (2) could not occur were not possible.

The spectra of the pyridine solutions of $NbCl_4$ and $NbBr_4$ at room temperature also are shown in Fig. 3. These spectra were found to be less complex than that of NbI_4 in pyridine, and certainly in the case of $NbCl_4$ (probably in the case of $NbBr_4$) indicated a single absorbing species in the solution. Since both complexes were observed to be non-electrolytes, the species are most likely $NbBr_4(py)_2$ and $NbCl_4(py)_2$, in accordance with the composition of the crystalline compounds. Interpretation of the spectra in terms of ligand field theory and electronic transitions involving niobium(IV) octahedrally coördinated, with either *cis* or *trans* molecular configuration and $4d^1$ electronic configuration, is clouded by the intensity of the observed absorption bands. For example, solutions of $NbCl_4$ gave λ_{max} 485 mμ, ϵ_{max} 1010 ± 50, and $NbBr_4$ solutions gave λ_{max} 483 mμ, ϵ_{max} 720 ± 50, λ_{max} 438 mμ, ϵ_{max} 680 ± 50. These extinction coefficients are larger than those expected for d–d ligand field transitions by a factor of 10 to 100, but are comparable in magnitude to those expected of charge transfer transitions. However, it is exceptional to observe charge transfer bands for complexes of this type in the visible region of the spectrum.

Charge transfer bands involving either chloride or bromide ligands in this region of the spectrum seem very unlikely. Such bands, however, may be attributed to ligand pyridine and have been discussed recently by Schläfer and König[18] for pyridine complexes of other metal halides. In the case of the niobium(IV) complexes, the transitions are probably either of the following types: (1) an electronic transition from a bonding π-M.O. formed by overlap of the Nb d_{xz} or d_{yz} atomic orbitals with the filled π-orbitals of pyridine, to a non-bonding orbital, say d_{xy} on niobium, or (2) a transition from a non-bonding orbital (d_{xy}) to an unoccupied antibonding M.O. composed mostly of the antibonding π-orbitals on pyridine. Schläfer and König considered only transitions of the second type for metal ions such as Ir(III), Cu(II), Co(II), or Mo(III) which have at least half-filled non-bonding orbitals. For metal ions of high charge and having fewer non-bonding electrons, transitions of type 1 should become more favorable. Examples of charge transfer transitions of type 1 have recently been demonstrated for vanadyl(IV)[19] and molybdenyl(V)[20] complexes, not containing pyridine, but rather, strongly π-bonded oxygen.

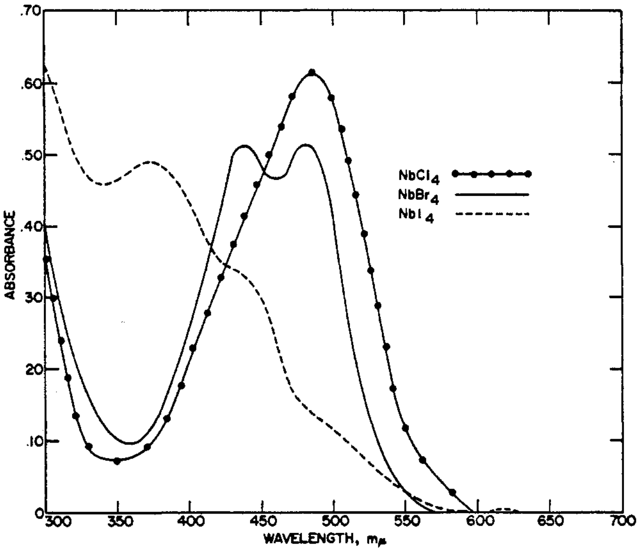

Fig. 3.—Visible spectra of pyridine solutions of the niobium(IV) halides at room temperature. Concentrations are: $NbCl_4$, 0.6 m*M*; $NbBr_4$, 0.7 m*M*; NbI_4, 0.9 m*M*.

The asymmetry of the band at 485 mμ in the spectra of $NbCl_4$ solutions suggests that there is another peak of much lower intensity on the low wave length side. If this is the case then the position and number of absorption bands in the spectra of $NbCl_4$ and $NbBr_4$ are similar, the spectra differing only in relative intensities of the bands. It thus appears that the complexes of $NbCl_4$ and $NbBr_4$ with pyridine have the same basic structure.

Whereas the spectra of solutions of $NbCl_4$ and $NbBr_4$ at room temperature were entirely stable for periods of up to 1 week, heating the solutions at 80 to 90° produced rapid and profound changes in the spectra. These changes proved to be irreversible and the spectra obtained after heating the solutions remained unchanged after cooling. In the spectra obtained after heating, peaks occurred at 398 and 440 mμ in the spectrum of the chloride, and at 408 and *ca.* 450 mμ (shoulder) in that of the bromide. The new peaks also showed anomalously high intensities of the type discussed above. Since the red form of $NbBr_4(py)_2$ was crystallized from solutions maintained at elevated temperature, it was thought that the changes in the spectrum on heating the solution were related to the formation of the red form. However, a solution prepared by dissolving red $NbBr_4(py)_2$ in pyridine at room temperature gave a spectrum substantially identical

---

(17) G. Kortüm and H. Wilski, *Z. physik. Chem.* (Leipzig), **202**, 35 (1953).

(18) H. L. Schläfer and E. König, *Z. physik. Chem.* (Frankfurt), **30**, 145 (1961).

(19) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(20) H. B. Gray and C. R. Hare, *ibid.*, **1**, 363 (1962).

TABLE III

MAGNETIC DATA FOR THE TETRAHALODI-(PYRIDINE)-NIOBIUM(IV) COMPLEXES

Complex	μ, B.M.	$N\alpha \times 10^6$, emμ mole^{-1} $N\alpha_t$	 $N\alpha_d$	 $N\alpha_p$
$NbCl_4(py)_2$	1.37	−60	−215	+155
$NbBr_4(py)_2$ (green)	1.26	−30	−255	+225
$NbBr_4(py)_2$ (red)	1.58	−100	−255	+155
$NbI_4(py)_2$	1.05	+100	−319	+419

with that of the green form. This result indicates the red and green forms of $NbBr_4(py)_2$ are not isomers, but rather, that the solids are dimorphic. Further work will be necessary to characterize the species associated with the spectra obtained after treatment of the solutions at high temperature.

The magnetic susceptibilities of the tetrahalodi-(pyridine)-niobium(IV) complexes were found to fit a simple Curie relationship over the temperature range −196 to 25°. The magnetic moments (μ) given in Table III were calculated directly from the slope of plots of χ (measured) *vs.* $1/T$. Also listed in the table are the values of $N\alpha_t$, the total temperature independent susceptibilities obtained from the intercepts of the above plots. Values for the temperature independent Van Vleck paramagnetism ($N\alpha_p$) were calculated from $N\alpha_t$ by subtracting the total diamagnetic contributions ($N\alpha_d$) of the atom cores[21] (for Nb, Cl, Br, and I) and the known susceptibility of pyridine.

Of special interest are the low magnetic moments found for each of the complexes and the trend to decreasing moment and increasing $N\alpha_p$ with increasing atomic number of the halogen in the complex. Thus, although the structures of the complexes are not known, it is possible to make some deductions about the structures from the trends in the observed magnetic properties. For example, in order for the magnetic moments to decrease in the direction indicated, the g-factors for the ground state of the complexes must decrease in the same direction. It may be assumed that the niobium(IV) in $NbX_4(py)_2$ has octahedral symmetry, the distortion of which will vary from one complex to another, depending on the net difference in ligand field strength between the pyridine and halogen ligands. Under the cubic field of the octahedral configuration the ground state for niobium(IV) is $^2T_{2g}$. Spin orbit coupling splits this term into the levels $^2T_{2g(1/2)}$ and $^2T_{2g(3/2)}$, the latter being lower.[22] It has $g = 0$ and thus no interaction with the external magnetic field. However, the asymmetric component (distortion) of the ligand field removes the degeneracy of $^2T_{2g}$ and gives either an orbital singlet or orbital doublet lying lowest, depending on the type of asymmetry imposed by the pyridine ligands. The g-factors thus should approach 2 as the magnitude of the asymmetric field component increases and the magnetic moments will tend toward the spin only value.[22]

The conclusion is made that the distortion from the octahedral symmetry caused by the pyridine ligands is greatest in the case of $NbCl_4(py)_2$, since the moment of this complex is nearest the spin-only value. Similarly, the distortion is least in the case of $NbI_4(py)_2$, with $NbBr_4(py)_2$ (green form) occupying an intermediate position. This result is just the opposite to that which would be expected on the basis of ligand field strengths obtained from the spectrochemical series, *i.e.*, I < Br < Cl < py. It was for this reason that the spectra were examined, but unfortunately, because of the uncertainty of interpretation of the spectra, direct information about the splitting of the energy levels was not obtained.

It should be noted that the moment given for red $NbBr_4(py)_2$ is not consistent with the above trend. Because of the unusual character, instability, and difficulty of obtaining pure samples of the red form the susceptibility data for it are more difficult to interpret. Thus it is doubtful that these data should be considered in the same set with that of the stable pyridine complexes.

It is tempting to attribute the apparent reversal of the spectrochemical series to the effects of π-bonding, or more correctly the combined action of σ- and π-bonding. McClure[23] has discussed a two dimensional spectrochemical series in terms of both σ- and π-bonding in substituted octahedral complexes. He concluded that the magnitude of splitting of spectral bands depended on both $\delta\sigma$ and $\delta\pi$, the difference in effective field strength between substituent ligands for σ-bonding and π-bonding, respectively. If $\delta\sigma$ and $\delta\pi$ have opposite signs the two effects are opposing and the splitting of spectral bands is smaller than expected on the basis of $\delta\sigma$ alone. Indeed, just the latter result is a logical deduction from the observed trend in the magnetic moments of $NbX_4(py)_2$. Thus, if pyridine is a strongly π-bonding ligand in these complexes, the order of π-bonding of the halogens is Cl < Br < I and is sufficient to offset the normal order in the spectrochemical series. This argument extends to corresponding complexes of tantalum(IV) which also exhibit magnetic moments decreasing with increasing atomic number of halogen in the complex, although the moments have lower values than those of the niobium compounds.

Acknowledgment.—The authors wish to thank Mr. John D. Greiner for his assistance in the determination and interpretation of the magnetic properties of the compounds prepared in the course of this work.

---

[21] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

[22] J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961, pp. 345 to 347.

[23] D. S. McClure, in "Advances in the Chemistry of Coordination Compounds," edited by S. Kirschner The Macmillan Co. New York N. Y., 1961, p. 498.