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The Preparation of Tantalum(IV) Bromide, Tantalum(IV) Iodide, and Pyridine Adducts of the Tantalum(IV) Halides[1a]

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The necessary conditions for preparation of $TaBr_4$ and TaI_4 by reduction of the pentahalides with tantalum or aluminum metal in a sealed tube under a controlled temperature gradient have been demonstrated. An unusual, but more fruitful synthesis of TaI_4 was devised from the reduction of TaI_5 with pyridine. X-Ray powder patterns of diamagnetic, isomorphous $TaCl_4$ and $TaBr_4$ were indexed on an orthorhombic unit cell of dimensions $a = 8.16$, $b = 8.92$, $c = 6.80$ Å. and $a = 8.58$, $b = 9.30$, $c = 7.21$ Å., respectively. The compounds $TaCl_4(C_5H_5N)_2$ and $TaBr_4(C_5H_5N)_2$ were prepared by the reaction of pyridine with the respective tetrahalides at room temperature. Unusually low magnetic moments of 0.69 and 0.43 B.M. were found for the chloride– and bromide–pyridine adducts, respectively.

Introduction

While the synthesis[2] and properties[3] of $TaCl_4$ have been studied extensively, very little work has been reported on other members of the tantalum(IV) halide family. For example, $TaBr_4$ has been mentioned as a minor product of the reduction of $TaBr_5$ with hydrogen,[4] but a method for its synthesis has not been described. Similarly, Rolsten[5] obtained a lower tantalum iodide from the vapors present in vessels used in the iodide purification of tantalum. It is doubtful that pure TaI_4 could be obtained under these conditions and the results of the present investigation indicate that the material described by Rolsten was really a mixture containing both TaI_5 and lower iodides. Thus one of the primary purposes of this work was to prepare and characterize these pure tetrahalides.

Previous studies[6] in this Laboratory indicated that the niobium(IV) halides formed dipyridine adducts with unusual and interesting properties. Because of the usual structural and chemical similarity between corresponding niobium and tantalum compounds, the reactions of the tantalum(IV) halides with pyridine also were studied. It had been demonstrated earlier that whereas the niobium(V) halides (Cl, Br, I) were reduced to the niobium(IV) derivatives in pyridine, the tantalum(V) halides (TaI_5 excepted) were not reduced.[7] This result added fuel to the fire of chemical differences between niobium and tantalum and made further study of the pyridine complexes of special interest.

Experimental

Materials.—High purity tantalum powder was obtained from the Metals Division of the National Research Corporation and was used in all tantalum halide preparations. The purity of this powder, as given by the producer, was 99.9+%.

Chlorine was obtained from the Matheson Company, Inc., in lecture size cylinders. The chlorine was vacuum distilled from the cylinder into the apparatus as needed for a preparation.

Reagent grade bromine was dried under vacuum over well outgassed P_4O_{10}. It was stored in a clean, evacuated flask under vacuum.

Eastman spectro-grade pyridine was dried first over outgassed calcium hydride and then vacuum distilled onto freshly outgassed barium oxide. It always was stored under vacuum.

Preparation of Tantalum(IV) Halides.—Tantalum(IV) chloride was obtained using the method of Schäfer and Kahlenberg.[3]

Anal. Calcd. for $TaCl_4$: Ta, 56.04; Cl, 43.96. Found: Ta, 56.20; Cl, 43.70.

Tantalum(IV) bromide initially was synthesized by reduction of $TaBr_5$ with tantalum powder in sealed, evacuated Vycor tubes, as shown in Fig. 1. Five g. of tantalum powder was placed in D and *ca.* 3 g. in B. The tube was evacuated and an excess of bromine was distilled into A. The tube then was sealed at E and placed in a furnace so that D was heated to 350 to 400°. As $TaBr_5$ was formed, it was sublimed into C. After 3 days, the excess bromine was frozen in A and the tube sealed at F and G.

The section of the apparatus labeled B and C was placed in a temperature gradient where B was heated to 630° and C heated to 300°. This temperature gradient was obtained by winding two ends of a furnace independently and using a stainless steel liner through the length of the furnace. It then was possible to adjust the temperature at either end independently of the other and maintain a smooth gradient along the entire length of the furnace. The temperature of 300° maintained the vapor pressure of $TaBr_5$ at 260 mm.[8] After 14 days, *ca.* 1–2 g. of a dark, crystalline product was obtained near the cool end of the tube. Reactions which were allowed to proceed over longer periods resulted in somewhat higher yields of the $TaBr_4$.

The tetrabromide was obtained more conveniently by reduction of $TaBr_5$ with aluminum foil. Aluminum foil was placed in one end of a Pyrex tube, *ca.* 14 in. in length, and an excess of freshly prepared $TaBr_5$ was added. The tube then was evacuated, sealed, and placed in a temperature gradient of 500° (Al) to 250° (*ca.* 60 mm. of $TaBr_5$). After 7 days 1–2 g. of a dark, crystalline substance was obtained near the cool end of the tube.

Anal. Calcd. for $TaBr_4$: Ta, 36.15; Br, 63.85. Found: Ta, 36.01; Br, 63.52.

In the initial attempts to prepare $TaBr_4$ by the reduction of $TaBr_5$ with tantalum powder, the reactions were performed in a sealed tube under a uniform temperature gradient where the section containing the tantalum was at 630° and that containing the $TaBr_5$ was at 400°. The latter temperature maintained a $TaBr_5$ pressure of *ca.* 4 atm. Under these conditions a gray-green, powdery product was deposited in the middle section of

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[1] (a) Contribution No. 1225. 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 J. C. Boatman to the Iowa State University in partial fulfillment of the requirements for the degree of Master of Science.

[2] (a) O. Ruff and F. Thomas, *Ber.*, **55B**, 1466 (1922); (b) H. Schäfer and L. Grau, *Z. anorg. allgem. Chem.*, **275**, 198 (1954).

[3] H. Schäfer and F. Kahlenberg, *ibid.*, **305**, 178 (1960).

[4] V. Gutmann and H. Tannenberger, *Monatsh.*, **87**, 769 (1956).

[5] R. F. Rolsten, *J. Am. Chem. Soc.*, **80**, 2952 (1958).

[6] R. E. McCarley and B. A. Torp, *Inorg. Chem.*, **2**, 540 (1963).

[7] 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.

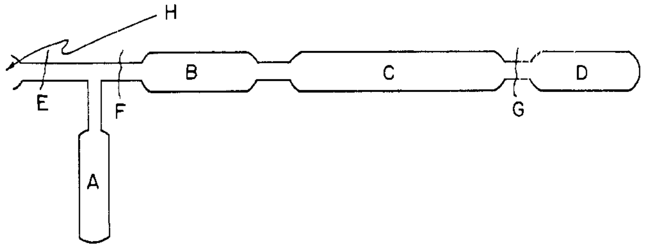

Fig. 1.—Vycor apparatus for the preparation of tantalum(IV) halides: A, halogen container; B, metal; C, pure tantalum(V) halide; D, metal; E, F, and G, sealing points; and H, to vacuum system.

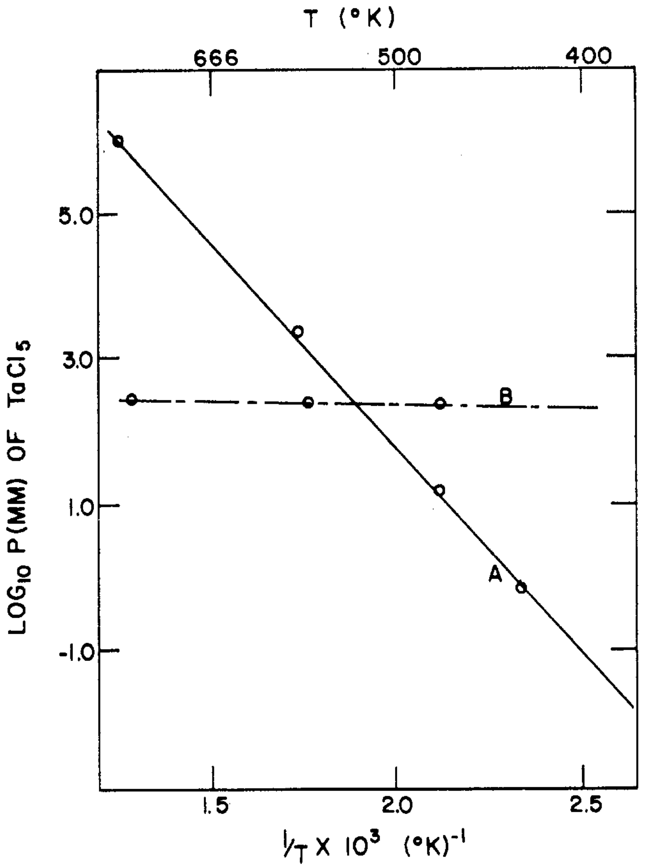

Fig. 2.—Log pressure of $TaCl_5$(g) over: A, $TaCl_4$(s); B, $TaCl_5$(s,l).

the tube at an intermediate temperature. The composition of this solid corresponded to $TaBr_{2.5}$ and indicated that a mixture of $TaBr_3$ and $TaBr_2$ was obtained.

It was found, however, that the latter product was not sufficiently volatile at 600° to account for its location in the reaction tube. Hence the conclusion was drawn that the material was transported down the tube as $TaBr_4$ *via* (1), but that after deposi-

$$Ta(s) + 4TaBr_5(g) = 5TaBr_4(g) \qquad (1)$$

tion of $TaBr_4$ at a lower temperature, *i.e.*, $630° > t > 400°$, a disproportionation reaction ensued *via*

$$2TaBr_4(s) = TaBr_3(s) + TaBr_5(g) \qquad (2)$$

or

$$3TaBr_4(s) = TaBr_2(s) + 2TaBr_5(g) \qquad (3)$$

In order to suppress the latter reactions it would be necessary to maintain a higher vapor pressure of $TaBr_5$ in the system. However, the higher vapor pressure can be attained in a system of the type used here only by simultaneously raising the temperature at the cool end of the reaction tube. The net result of the competing vaporization processes can be deduced from Fig. 2, where the log of the vapor pressure[8] of pure $TaCl_5$ and that of $TaCl_5$ resulting from the disproportionation[2] of $TaCl_4$(s) is plotted against reciprocal temperature over the experimental temperature range. Inspection of the two curves shows that above a critical temperature of *ca.* 280° (the point of intersection of the two curves) the pressure of $TaCl_5$ required to suppress a disproportionation such as that shown in reaction 2 or 3 would be greater than the vapor pressure of $TaCl_5$ at the same temperature. Thus in a reaction of the type illustrated by eq. 1, $TaCl_4$ could not be obtained as a stable product at any temperature greater than *ca.* 280°. However, below this critical temperature $TaCl_4$ should be the stable product.

Even though the pressures of $TaBr_5$ resulting from the disproportionation of $TaBr_4$(s) over the experimental temperature range were not known, the analysis of the conditions necessary for the preparation of $TaCl_4$ was applied to the preparation of the bromide. Indeed, when temperatures below *ca.* 330° were chosen at the $TaBr_5$ end of the tube crystalline $TaBr_4$ was obtained; above this temperature the lower bromides were obtained. Thus the "critical" temperature at the cool end of the reaction tube for successful preparation of $TaBr_4$ was established as *ca.* 330°.

Tantalum(IV) iodide was obtained from TaI_5 by two different methods, one utilizing aluminum as the reducing agent and the other pyridine.

The first method paralleled the procedure utilized in the preparation of $TaBr_4$. Tantalum(V) iodide was prepared first by placing tantalum powder and the calculated amount of iodine in a Pyrex tube, which then was evacuated and sealed. The tube then was placed in a temperature gradient of 400° (Ta end) to 180° (1 atm. of I_2) for 48 hr. Next an excess of the TaI_5 was placed in a Pyrex tube containing 0.1–0.2 g. of aluminum foil. The tube and its contents were placed on a vacuum manifold and evacuated to *ca.* 10^{-5} mm. and sealed. It then was placed in a temperature gradient of 500° (Al end) to 350° (*ca.* 16 mm. of TaI_5 pressure[9]). After 7 days, 5 g. of a lustrous, gray crystalline deposit was found in a zone which was well separated from the excess TaI_5.

Anal. Calcd. for TaI_4: Ta, 26.29; I, 73.71. Found: Ta, 26.72; I, 74.31.

An argument similar to that given for establishment of the optimum temperatures necessary for the preparation of $TaBr_4$ was used to establish the conditions required for the preparation of TaI_4 by aluminum reduction of TaI_5. In order to prevent disproportionation of TaI_4 after deposition a temperature of only 350° was maintained at the cool end of the reaction tube, but this temperature made the synthesis of TaI_4 impractically slow since it maintained a TaI_5 vapor pressure of only *ca.* 16 mm. during the reaction. For this reason the alternate method given below was developed.

The second method utilized the decomposition of the pyridine adduct of TaI_4, the preparation of which is described in the following section. The pyridine adduct (5–10 g.) was placed in a tube, which was fitted with a side arm condenser; the tube then was evacuated and sealed. Subsequently the complex was heated to 200° for 2 days while evolved pyridine was collected in the side arm at −78°. The pyridine then was frozen with liquid N_2 and sealed off from the black, powdered TaI_4, which was obtained in virtually quantitative yield.

Anal. Found: Ta, 26.03; I, 73.43.

Reductions of TaI_5 with tantalum also were attempted using the sealed tube–temperature gradient technique. Using a temperature gradient of 630° (Ta) and 530 to 585° (from 1 to 3 atm. of TaI_5 pressure), a lower iodide, TaI_3, invariably was obtained as the sole product.

Anal. Calcd. for TaI_3: Ta, 32.22; I, 67.78. Found: Ta, 32.38; I, 67.53.

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(8) K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, S223 (1949).

(9) K. M. Alexander and F. Fairbrother, *ibid.*, 2472 (1949).

Tetrahalodi-(pyridine)-tantalum(IV) Complexes.—The complexes of tantalum(IV) chloride and bromide were prepared by stirring, in evacuated flasks, weighed samples of the tetrahalides with excess pyridine. The times required for complete conversion of the tetrahalides varied from 36 to 48 hr. depending upon the size of the initial tetrahalide sample. After the conversions into the complexes were complete, the pyridine was vacuum distilled from the flasks and the powdered residues were dried under vacuum (*ca.* 10^{-5} mm.) for 48 hr. The complexes then were stored in tightly capped bottles in a drybox.

Anal. Calcd. for $TaCl_4(py)_2$: Ta, 37.61; Cl, 29.51; py, 32.88. Found: Ta, 37.22; Cl, 29.17; py, 32.72. Calcd. for $TaBr_4(py)_2$: Ta, 27.47; Br, 48.51; py, 24.02. Found: Ta, 27.40; Br, 48.32; py, 23.82.

A method for the preparation of the pyridine complex of TaI_4 was suggested by the reduction of TaI_5 in pyridine,[7] which proceeds according to eq. 4 and where pyridine functions both as

$$2TaI_5 + 5py = 2TaI_4(py)_2 + pyI_2 \qquad (4)$$

solvent and ligand. Thus, 5–10 g. of TaI_5, in a sealed evacuated flask, was stirred with 50 ml. of pyridine for 3 days at room temperature. The excess pyridine was removed by vacuum distillation, and the red-black residue transferred to a modified Soxhlet extractor, where it was leached continuously with pyridine until the washings became colorless. Extraction with pyridine was desirable because it not only removed the pyridine–iodine adduct but also aided in driving reaction 4 to completion. The desired rust-brown product remained on the filter after the extraction, while a residue containing iodine was recovered from the solvent flask.

Anal. Calcd. for $TaI_4(py)_2$: Ta, 21.37; I, 59.94; py, 18.68. Found: Ta, 21.75; I, 61.94; py, 16.13.

Although the analytical data on this product indicated the composition to be $TaI_{4.06}(py)_{1.70}$, the X-ray powder pattern of the solid was virtually identical with that given by $NbI_4(py)_2$.[6] Lines attributable to TaI_4 or TaI_5 were not observed in the pattern. However, in order to account for the observed stoichiometry of the complex, a mixture containing from 6 to 10% of unreduced TaI_5 may be assumed. For example, a mixture containing 10% TaI_5 and 90% $TaI_4(py)_2$ would result in an overall composition for the mixture of $TaI_{4.1}(py)_{1.8}$, a value in reasonable agreement with the observed composition. It is probable that TaI_5 in amounts up to 10–15% would escape detection in the X-ray diffraction pattern. Other experiments to prepare stoichiometric $TaI_4(py)_2$ were less successful than that given above.

X-Ray diffraction data for the three tantalum(IV) halide–pyridine complexes are given in Table I. These data may be compared with the X-ray data for the corresponding niobium(IV) complexes which were given in another paper.[6]

X-Ray Data.—All X-ray data were obtained using a Debye-Scherrer 114.59-mm. powder camera. The samples were packed in 0.2-mm. glass capillaries under an inert atmosphere and sealed immediately. The samples were exposed to Cu Kα radiation, using a Ni filter, for 14 to 24 hr. depending upon the sample.

Magnetic Susceptibilities.—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.

Analytical.—All samples were hydrolyzed in a concentrated ammonia solution which was boiled when it was required for rapid hydrolysis. The precipitated tantalum(V) oxide was filtered, ignited, and weighed as Ta_2O_5. Halide ion was determined either by means of Volhard titration or by precipitation as silver halide and then weighing.

The pyridine analysis was accomplished by steam distillation of pyridine, which was liberated from the complex in concentrated sodium hydroxide, into glacial acetic acid. The wet glacial acetic acid solution then was dried with acetic anhydride. This was accomplished by allowing the capped solution to stand overnight, or by boiling in a water bath for 1 hr. The anhydrous solution then was titrated potentiometrically with a standard solution of perchloric acid in glacial acetic acid.[10] The electrodes for this titration were a standard Beckman glass electrode and a calomel cell filled with a saturated solution of LiCl in glacial acetic acid. This procedure proved quite satisfactory for the determination of pyridine complexed with niobium and tantalum halides. The reliability of the procedure was confirmed by determinations of pyridine in aqueous solutions containing known amounts of the base under the same conditions used for analysis of the pyridine complexes. A maximum error of 2% in the pyridine analysis was found for the procedure.

TABLE I

X-RAY POWDER DIFFRACTION DATA OF PYRIDINE COMPLEXES OF THE TANTALUM(IV) HALIDES[a]

$TaCl_4(py)_2$	$TaBr_4(py)_2$	$TaI_4(py)_2$
6.48(10)	6.61(10)	6.75(10)
6.11(10)	6.29(5)	5.59(2)
5.16(8)	5.28(5)	4.35(1)
4.14(5)	4.22(4)	4.16(1)
3.95(1)	4.04(1)	3.93(8)
3.85(5)	3.87(10)	3.84(6)
3.71(3)	3.25(7)	3.60(1)
3.14(6)	2.86(1)	3.46(7)
2.90(1)	2.64(9)	3.30(3)
2.68(3)	2.53(5)	2.78(9)
2.57(1)	2.42(3)	2.58(7)
2.50(7)	2.11(1)	2.40(1)
2.43(6)	2.06(2)	2.19(4)
2.35(1)	2.01(3)	2.15(3)
2.03(3)	1.94(1)	2.01(3)
1.96(2)	1.82(1)	1.97(4)
1.87(2)	1.76(2)	1.93(3)
1.76(2)	1.70(1)	1.84(2)
1.68(2)	1.51(1)	1.80(2)
1.53(2)		1.59(1)
1.48(2)		1.56(1)
1.41(2)		1.40(1)
		1.36(1)

[a] Relative intensities are given in parentheses and were estimated visually relative to a value of 10 for the most intense line.

Results and Discussion

Tantalum(IV) Halides.—It is evident from the low yields (1–2 g.) and long reaction times needed that the synthesis of $TaBr_4$ *via* tantalum or aluminum reduction of $TaBr_5$ is not a fruitful method if large quantities of the tetrabromide are desired. However, the method is important because it provides a means of preparation at elevated temperatures under conditions where a sufficient pressure of $TaBr_5$ can be maintained to prevent disproportionation of the product. As indicated in the Experimental section it was noted that in the reduction of $TaBr_5$ with tantalum if the temperature at the cool end of the reaction tube was maintained above *ca.* 330° the solid product of composition $TaBr_{2.5}$ was obtained. It may be deduced from this condition that the vapor pressure of $TaBr_5$ and the pressure of $TaBr_5$ over $TaBr_4$ (due to disproportionation) become equal at *ca.* 330° and 550 mm. of $TaBr_5(g)$.[8] Above 330° the vapor pressure of $TaBr_5$ is always less than the equilibrium disproportionation pressure and only the lower bromides can be obtained.

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

Table II

Observed and Calculated *d*-Spacings for TaCl$_4$ and TaBr$_4$

	TaCl$_4$		TaBr$_4$	
hkl	*d* (calcd.)	*d* (obsd.)[a]	*d* (calcd.)	*d* (obsd.)[a]
110	6.02	6.04 (10)	6.30	6.22 (10)
020	4.46	4.46 (8)	4.65	4.68 (9)
111	4.46	4.46 (8)	...	...
200	4.08	4.08 (8)	4.29	4.31 (8)
002	3.40	3.40 (5)	...	...
220	3.02	3.06 (1)	...	...
121	...	...	3.56	3.57 (1)
030	2.97	2.95 (5)	3.10	3.11 (4)
221	2.76	2.76 (1)	...	...
031, 022	2.72	2.71 (9)	2.85	2.84 (10)
202	2.61	2.62 (7)	2.76	2.77 (10)
131, 122	2.58	2.57 (3)	2.70	2.70 (2)
033, 231	2.27	2.27 (1)	...	...
040	2.23	2.23 (5)	...	...
132, 103	2.16	2.17 (3)	...	...
140	2.15	2.14 (3)	...	...
312	2.07	2.08 (1)	...	...
141	2.05	2.06 (2)	...	...
032	...	...	2.35	2.35 (7)
302	...	...	2.24	2.25 (4)
400	2.04	2.04 (5)	2.15	2.15 (10)
203, 410	1.98	1.98 (1)	...	...
331	1.93	1.93 (1)	...	...
411	...	...	2.00	1.99 (1)
420	1.87	1.87 (3)	1.95	1.96 (1)
142	1.82	1.83 (1)	...	...
402	1.75	1.75 (5)	...	...
303	...	...	1.84	1.84 (6)
313	1.71	1.71 (2)	1.81	1.82 (4)
242	1.69	1.70 (2)	...	...
500	1.63	1.64 (3)	...	...
510	1.60	1.61 (4)	1.69	1.69 (5)
403	...	...	1.59	1.60 (5)
503	...	...	1.54	1.56 (3)

[a] All intensities, as shown in parentheses, were estimated visually relative to a value of 10 for the most intense line.

The X-ray data showed TaBr$_4$ to be isomorphous with TaCl$_4$ and NbBr$_4$,[6] and also probably isomorphous with MoBr$_4$[11] and WBr$_4$.[12] Lattice constants were calculated for TaBr$_4$ from single crystal data of NbBr$_4$, and were found to be a = 9.58, b = 9.30, and c = 7.21 Å. A comparison of the observed and calculated *d*-spacings is shown in Table II.

Lattice constants also were determined for TaCl$_4$ from single crystal data of NbCl$_4$ and were found to be a = 8.16, b = 8.92, and c = 6.80 Å. A comparison of the observed and calculated *d*-spacings also is given in Table II. Both TaCl$_4$ and TaBr$_4$ are of the orthohombic crystal system.

Rolsten[5] reported that a green solution resulted when a sample of TaI$_4$ was added to water, but further investigation in this Laboratory has shown that such a green solution is formed only by a lower iodide.[13] Neither TaI$_4$, prepared by the methods given above, nor TaI$_3$ dissolved in water to produce a green solution. Rather, TaI$_4$ hydrolyzed rapidly with formation of a hydrous brown oxide, whereas TaI$_3$ appeared to be inert to water at room temperature. The composition of the lower iodide which produces the green solution is not known, but further work in this regard has been undertaken.

Table III

X-Ray Diffraction Data for TaI$_4$

TaI$_4$ (by Al reduction)		TaI$_4$ (by decomposition of pyridine complex)	
d (obsd.), Å.	*d* (obsd.), Å.	*d* (obsd.), Å.	*d* (obsd.), Å.
5.82 (2)[a]	2.66 (2)[a]	5.99 (5)[a]	1.92 (5)[a]
5.58 (4)	2.55 (1)	4.48 (1)	1.88 (1)
5.27 (4)	2.51 (1)	4.07 (5)	1.85 (4)
4.03 (5)	2.32 (1)	3.95 (3)	1.71 (2)
3.64 (3)	2.25 (1)	3.86 (3)	1.69 (2)
3.45 (4)	2.20 (2)	3.08 (10)	1.66 (4)
3.28 (7)	2.17 (2)	3.00 (10)	1.63 (2)
3.18 (10)	2.09 (3)	2.41 (5)	1.50 (2)
3.07 (8)	2.07 (3)	2.36 (4)	1.24 (2)
2.96 (5)	1.96 (3)	1.99 (10)	1.23 (2)
2.78 (3)	1.83 (1)		

[a] Intensities are given in parentheses and were estimated visually relative to a value of 10 for the most intense line.

An interesting result of this study on the preparation of TaI$_4$ is the fact that the two methods given above apparently produced different crystalline forms. It was difficult to obtain good powder diffraction patterns of the solids, but the results showed clearly that different crystalline modifications of TaI$_4$ were obtained from the two methods. Diffraction data for the two products are presented in Table III.

Neither of the patterns given in Table III could be indexed on the orthorhombic cell and space group given by Dahl and Wampler[14] for α-NbI$_4$. However, the occurrence of two modifications of TaI$_4$ does seem to mimic the existence of more than one form of NbI$_4$.[15] If a comparison of these iodides can be made, the TaI$_4$ formed by thermal decomposition of the pyridine adduct TaI$_{4.1}$(py)$_{1.7}$ at 200° should correspond to α-NbI$_4$, while the TaI$_4$ deposited at higher temperatures during reduction of TaI$_5$ by aluminum should correspond to one of the high temperature modifications of NbI$_4$.

Tetrahalodi-(pyridine)-tantalum(IV) Complexes.—The brick-red chloride adduct and the light brown bromide adduct were both relatively insoluble in the solvent pyridine. Both complexes appeared to be more resistant to hydrolysis than the respective tetrahalides. X-Ray powder diffraction patterns of both the bromide and chloride complexes showed them to be isomorphous with their analogous niobium(IV) complexes.[6]

Magnetic susceptibilities of the compounds TaX$_4$(py)$_2$ were of considerable interest because of a previous trend found in the magnetic moments of the corresponding niobium(IV) compounds.[6] It also was pertinent to determine if the usual diamagnetism (and possible metal–metal bonding) associated with the tantalum(IV) halides was retained on formation of the pyridine complexes. However, both TaCl$_4$(py)$_2$ and TaBr$_4$(py)$_2$ proved to be paramagnetic, showing that the

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(11) P. J. H. Carnell and R. E. McCarley, unpublished research.

(12) R. E. McCarley and T. M. Brown, to be published.

(13) R. E. McCarley, J. C. Boatman, and P. J. Kuhn, unpublished research.

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

(15) P. W. Seabaugh, "Physical Properties of Niobium Halides," Ph.D. Thesis, Ames, Iowa, Library, Iowa State University of Science and Technology, 1961.

TABLE IV

MAGNETIC PROPERTIES OF $TaCl_4(py)_2$ and $TaBr_4(py)_2$

Substance	μ, B.M.	$N\alpha_t \times 10^6$	$N\alpha_d \times 10^6$	$N\alpha_p \times 10^6$
$TaCl_4(py)_2$	0.69	− 5	−219	+214
$TaBr_4(py)_2$	0.43	−20	−259	+239

tantalum(IV) ion possessed the expected $5d^1$ configuration.

Measurements from −196 to 25° showed that the susceptibilities of the chloride and bromide complexes followed the simple Curie behavior. The magnetic moments μ were calculated directly from the slope of the straight line resulting from a plot of χ (measd.) *vs.* $1/T$. Also, the total temperature-independent susceptibility $N\alpha_t$ was obtained from the intercept of the plot at $1/T = 0$. Thus the total temperature-independent paramagnetism $N\alpha_p$ was calculated by subtraction of $N\alpha_d$, the total diamagnetic core contributions[16] of Ta, Cl, or Br, and pyridine. The results of these calculations are given in Table IV. Magnetic susceptibilities were not obtained for the TaI_4–pyridine complex since the purity of the compound was uncertain.

The low magnetic moments exhibited by these tantalum compounds were expected by analogy with the corresponding niobium(IV) compounds,[6] with which the tantalum derivatives are isomorphous. In this respect, the lower moments of the tantalum compounds must be a result of much larger spin-orbit coupling constants for Ta(IV).

In a manner similar to that discussed previously,[6] the lower moment of $TaBr_4(py)_2$ relative to that of $TaCl_4(py)_2$ gives evidence for strong π-bonding in these compounds and indicates a reversal of the normal spectrochemical order of the halide complexes. That is, the departure from true octahedral symmetry about the Ta(IV) must be greatest in the case of $TaCl_4(py)_2$. Ligand field theory predicts that the magnetic moments should approach the spin-only value more closely as the orbital degeneracy of the ground state is removed by the increasing magnitude of the asymmetric component of the ligand field.[17] From the normal order of the ligands in the spectrochemical series (Br < Cl < py), however, the largest asymmetric field component and highest magnetic moment would be realized in $TaBr_4(py)_2$. Since the latter is not the case, the trend in the magnetic moments indicates a reverse order for the halide ligands, *i.e.*, Cl < Br < py.

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

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

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The Preparation and Properties of Some Pentachloroalkoxo Complexes of Niobium(IV)

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A number of complexes of the type $(BH)_2Nb(OR)Cl_5$ have been prepared by electrolytic reduction of $NbCl_5$ in HCl-saturated alcohols, followed by the addition of alcoholic solutions of BH^+ ions (B is an amine such as CH_3NH_2, pyridine, quinoline, etc.). All compounds show normal, spin-only paramagnetism for the d^1 ion. Spectra of aromatic "-inium" salts are complicated and suggest that there is an interaction with the $Nb(OR)Cl_5^-$ ion. The interaction seems to result in weakening of the aromatic C–H and the alkoxo C–O bonds and a distortion of the complex ion to greater tetragonality.

In an earlier communication,[1] we reported the preparation of a series of compounds containing the pentachloroalkoxoniobate(IV) ion and we described, in particular, pyridinium pentachloromethoxoniobate(IV). That work has been extended to include the preparation and properties of dimethyl- and tetramethylammonium, picolinium, and quinolinium isoquinolinium and N-methylquinolinium salts as well as pyridinium salts and to include ethoxo- and isopropoxo- as well as methoxo- anions.

The literature contains a number of reports of electrolytically reduced niobium solutions,[2–5] but isolation of definite, authenticicated compounds from aqueous electrolyses was not established until Golibersuch and Young[6] succeeded in obtaining several crystalline sodium, potassium, and ammonium niobium sulfates which contained niobium in the average oxidation states of 3.33 and 3.67.

Because of the difficulty of preparing simple complexes of niobium(III) or (IV) by electrolysis of

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[1] R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **1**, 971 (1962).

[2] F. Ott, *Z. Elektrochem.*, **18**, 349 (1912).

[3] E. Grube and H. L. Grube, *ibid.*, **44**, 771 (1938).

[4] A. Stahler, *Ber.*, **47**, 841 (1914).

[5] S. J. Kiehl and D. Hart, *J. Am. Chem. Soc.*, **50**, 1614 (1928).

[6] E. H. Golibersuch and R. C. Young, *ibid.*, **71**, 2402 (1949).