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.

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.

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(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).

aqueous solutions, we undertook to investigate electrolysis of alcoholic HCl solutions of niobium(V) and to measure spectra and magnetic properties of the products so obtained.

Experimental

Materials.—Niobium pentachloride was obtained as a gift from Diamond Alkali Company and used without further purification. Niobium pentabromide was prepared by elementary synthesis. Niobium sheet was obtained from Fairmont Chemical Company. The reaction was accomplished in a sealed tube constructed so that the liquid bromine was at room temperature while the metal was held to 400°. The criterion for purity was the absence of any orange niobium oxybromide.

Methyl alcohol was dried by reaction with magnesium and subsequent distillation. Ethyl and isopropyl alcohols were dried by reaction with sodium and were distilled. Chloroform was dried over calcium chloride and distilled prior to use.

Anhydrous hydrogen chloride and hydrogen bromide in cylinders were obtained from the Matheson Company and used without further purification. Nitrogen was purified by passing General Dynamics oil-pumped nitrogen over copper turnings at 500°. It then was dried by bubbling through concentrated sulfuric acid and passing over anhydrous magnesium perchlorate.

Tetramethylammonium chloride, pyridine, quinoline, and isoquinoline were Eastman White Label grade. The tetramethylammonium chloride was first dried at 80°. Pyridine was dried by distillation from barium oxide and was stored in a dry container.

Alcoholic solutions of dimethylammonium chloride were prepared by allowing a known amount of anhydrous dimethylamine to be absorbed in the alcohol saturated with HCl.

N-Methylpyridinium iodide was prepared by allowing stoichiometric quantities of pyridine and methyl iodide to react. Two recrystallizations from ethyl alcohol–benzene mixtures gave yellow acicular crystals, m.p. 116.5° (lit.[7] 118°). N-Methylquinolinium iodide was prepared and purified similarly to yield white acicular crystals, m.p. 145° (lit.[8] 144.5°).

Magnetic Moment Measurements.—Magnetic susceptibilities were measured by the Gouy method using distilled water as the standard. The apparatus and techniques in low temperature studies are those which were used by Vander Vennen.[9] Pascal's constants[10] were used to correct the measured susceptibilities for the diamagnetism of the cations and ligands, except for pyridinium and quinolinium ions. The values for these ions were obtained from Holm and Cotton.[11] The results are shown in Table I, and in all cases the susceptibilities followed the Curie–Weiss law.

Spectroscopic Measurements.—The complete infrared spectra of the complexes were obtained with Nujol mulls and use of a Perkin-Elmer Model 21 spectrophotometer. The spectra from 2400–3600 cm.$^{-1}$ for the quinolinium compounds were obtained with perfluorokerosene mulls and a Beckman IR-7 spectrophotometer. The mulls were prepared in a drybox under a nitrogen atmosphere.

The visible reflectance spectra were obtained with a Bausch and Lomb spectrophotometer with a reflectance attachment. $MgCO_3$ was used as a standard. In order to prevent oxidation of the samples, they were ground with mineral oil and spread between two circular microscope cover glasses.

Elementary Analyses.—Samples of the complexes were oxidized in very dilute nitric acid, made basic with aqueous ammonia, and digested on a steam bath for several hours. The solutions were then adjusted to pH 1 with nitric acid and were filtered to remove the hydrous niobium pentoxide. Niobium was determined gravimetrically by ignition of the hydrous oxide. Chloride or bromide was determined by potentiometric titration of the filtrate with $AgNO_3$.

Carbon and hydrogen analyses were performed by Spang Microanalytical Laboratory.

The oxidation state was confirmed on a few samples by oxidation with $K_2Cr_2O_7$, followed by amperometric back titration of the excess Cr(VI) with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Later studies showed that the magnetic moment of niobium(IV) in these compounds was very close to the spin-only value for a d^1 ion, so that this property served to confirm the oxidation state.

Electrolysis Apparatus.—The electrolysis vessel consisted of a 125-ml. erlenmeyer flask with a ground glass top. The flask was fitted with a two-way stopcock on the bottom and a bent side arm which contained a fine porosity fritted glass disk. The vertical portion of the side arm served as the anode compartment. The level of the mercury pool cathode could be adjusted by a leveling bulb which was connected to one arm of the two-way stopcock by a short piece of flexible tubing. The anode compartment contained the appropriate alcohol saturated with HCl and a short piece of carbon rod which served as the anode. The solution was stirred during the electrolysis by means of bubbling dry, purified nitrogen through the electrolyte and allowing it to escape through an opening in the top of the flask. The nitrogen also served to exclude air and moisture.

Preparation of Compounds. Methoxo Complexes.—The preparation and properties of pyridinium pentachloromethoxoniobate (IV) were described briefly in the earlier communication.[1] A more complete description is given here and applies to the preparation of all the complexes. A solution of Nb(IV) is prepared by the electrolytic reduction of $NbCl_5$ (4.05 g., 0.015 mole) in 25 ml. of anhydrous methyl alcohol saturated with HCl. The potential is adjusted so that a current of 0.075 amp. is maintained throughout the electrolysis. The solution rapidly becomes wine-red and then changes to a deep brown after several hours. No hydrogen evolution is noted until about the theoretical time for the one-electron reduction. Concurrently, the thin layer of solution between the flask and the meniscus of the mercury becomes yellow-brown while the bulk of the solution remains dark brown. Titration experiments with portions of the solution show that the reduction is complete at this point. (On one occasion, the period of electrolysis was extended by 300%, but no further reduction of the niobium was noted.)

The mercury then is removed and the solution drained into a flask containing slightly more than the stoichiometric quantity of pyridine in hot methyl alcohol saturated with HCl. The compound, which results after several hours of cooling, is obtained as a red-brown, spiny, crystalline agglomerate. Filtration is accomplished under a nitrogen atmosphere. The crystals are washed with three 20-ml. portions of chloroform, and dried by continuous pumping for 24 hr. *Anal.* Calcd. for $(C_5H_6N)_2Nb(OCH_3)Cl_5$: C, 28.61; H, 3.27; Cl, 38.45; Nb, 20.13. Found: C, 28.67; H, 3.30; Cl, 38.21; Nb, 20.21. Oxidation state: 4.03.

When cold methyl alcohol is substituted for chloroform, the observed chloride to niobium ratio is only 4.88, indicating some solvolysis had occurred.

Tetramethylammonium Pentachloromethoxoniobate(IV).—Pink crystals after a few minutes. *Anal.* Calcd.: Cl, 39.50; Nb, 20.68. Found: Cl, 39.1; Nb, 20.77.

Quinolinium Pentachloromethoxoniobate(IV).—Violet crystals after 20 min. *Anal.* Calcd.: Cl, 31.61; Nb, 16.55. Found: Cl, 31.2; Nb, 16.71.

Isoquinolinium Pentachloromethoxoniobate(IV).—Red crystals after 10 min. *Anal.* Calcd.: Cl, 31.61; Nb, 16.55. Found: Cl, 31.2; Nb, 16.58.

Ethoxo Complexes. Dimethylammonium Pentachloroethoxoniobate(IV).—Peach needles within 1 min. *Anal.* Calcd.: Cl, 43.56; Nb, 22.80. Found: Cl, 43.5; Nb, 22.87.

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[7] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, p. 275.

[8] Reference 7, p. 303.

[9] R. E. Vander Vennen, Ph.D. Thesis, Michigan State University, 954.

[10] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. ewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, p. 403.

[11] R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 790 (1959).

Pyridinium Pentachloroethoxoniobate(IV).—Orange crystals within a few minutes. *Anal.* Calcd.: C, 30.30; H, 3.56; Cl, 37.33; Nb, 19.54. Found: C, 30.62; H, 3.71; Cl, 37.21; Nb, 19.41.

N-Methylpyridinium Pentachloroethoxoniobate(IV).—Red crystals after 5 min. *Anal.* Calcd.: Cl, 35.25. Found: Cl, 35.0.

4-Picolinium Pentachloroethoxoniobate(IV).—Orange crystalline polyhedra after a few minutes. *Anal.* Calcd.: Cl, 35.25; Nb, 18.45. Found: Cl, 35.5; Nb, 18.59.

Quinolinium Pentachloroethoxoniobate(IV).—Crystallization of this violet compound is initiated by cooling at −77° until one crystal forms, then the solution is held at −10° for several hours. *Anal.* Calcd.: C, 42.91; H, 3.79; Cl, 30.80; Nb, 16.12. Found: C, 42.88; H, 3.67; Cl, 30.44; Nb, 15.73.

N-Methylquinolinium Pentachloroethoxoniobate(IV).—Violet crystals after 10 min. *Anal.* Calcd.: Cl, 29.40. Found: Cl, 29.5.

Isopropoxo Complexes. Tetramethylammonium Pentachloroisopropoxoniobate(IV).—Pink, curdy, precipitate immediately. This was not investigated further.

Pyridinium Pentachloroisopropoxoniobate(IV).—Orange powder forms immediately. *Anal.* Calcd.: Cl, 36.25; Nb, 18.98. Found: Cl, 35.9; Nb, 19.10.

Quinolinium Pentachloroisopropoxoniobate(IV).—Violet powder forms immediately. *Anal.* Calcd.: Cl, 30.11; Nb, 15.76. Found: Cl, 30.0; Nb, 15.86.

Attempts to Prepare Analogous Bromo Complexes.—Several attempts to prepare compounds containing the $Nb(OC_2H_5)Br_5^{-2}$ ion failed, with the methods described above. Green crystalline substances were obtained with no definite bromide to niobium ratio. For example, the material containing pyridinium ion had a Br/Nb ratio of 5.74. Significantly, the infrared spectrum showed no alkoxo groups to be present.

Attempts to Prepare Compounds Containing the $NbOCl_5^{-3}$ Ion.—Several attempts to prepare compounds of this class have failed. Two basic methods were tried and will be described.

When a 95% ethyl alcohol solution (saturated with HCl) of $NbCl_5$ (0.6 *M*) was electrolyzed and added to a stoichiometric quantity of pyridine in the same solvent, the product was $(C_5H_6N)_2Nb(OC_2H_5)Cl_5$. This was verified by its infrared spectrum and by analyses. *Anal.* Calcd.: Cl, 37.33. Found: Cl, 36.9.

When the hydrolysis of several of the alkoxo compounds was attempted with aqueous HCl (oxygen-free) in the presence of stoichiometric quantities of the organic base, considerable oxidation always occurred even when extreme precautions were taken to exclude oxygen.

Results and Discussion

The pentachloroalkoxoniobate(IV) complexes have been prepared and identified. One previous example $(pyH)_2Zr(OC_6H_5)Cl_5$ is known.[12]

Magnetic susceptibilities of three compounds: pyridinium pentachloromethoxoniobate(IV), quinolinium pentachloroethoxoniobate(IV), and quinolinium pentachloroisopropoxoniobate(IV) were measured as a function of temperature and the results are given in Table I. All obeyed the Curie–Weiss law and the moments corresponded to spin-only moments for a d^1 ion.

Infrared spectra reveal no OH absorption and all compounds show a band at about 1100 cm.$^{-1}$ which is characteristic of the C–O stretching vibration. Exact frequencies are: $((CH_3)_4N)_2Nb(OCH_3)Cl_5$, 1130 cm.$^{-1}$; $(pyH)_2Nb(OCH_3)Cl_5$, 1095; $(QuH)_2Nb(OCH_3)Cl_5$, 1110; $((CH_3)_2NH)_2Nb(OC_2H_5)Cl_5$, 1070 and 1100; $(pyH)_2Nb(OC_2H_5)Cl_5$, 1070 and 1090; $(QuH)_2Nb(OC_2H_5)Cl_5$, 1070 and 1090; and $(QuH)_2Nb(O(i\text{-}C_3H_7))Cl_5$, 1030 and 1100.

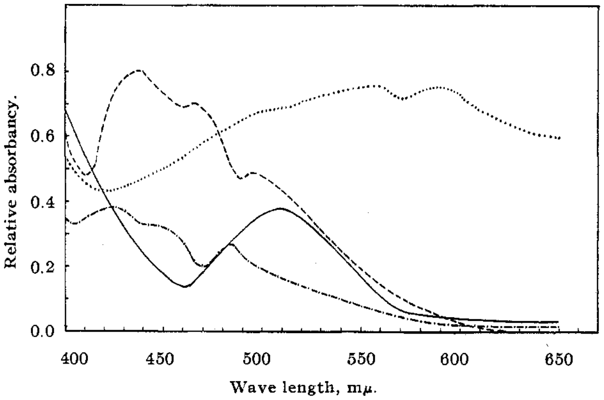

Fig. 1.—Visible reflectance spectra of some solid pentachloroethoxoniobates(IV): ———, $(CH_3NH_2)_2Nb(OC_2H_5)Cl_5$; – – – –, $(pyH)_2Nb(OC_2H_5)Cl_5$; – · – · –, $(4\text{-}picH)_2Nb(OC_2H_5)Cl_5$; . . . . . ., $(QuH)_2Nb(OC_2H_5)Cl_5$.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF SOME PENTACHLOROALKOXONIOBATES AS A FUNCTION OF TEMPERATURE

Compound	Temp., °A.	Susceptibility, $\chi'_M \times 10^6$	θ, °A.	μ_{eff}
$(pyH)_2Nb(OCH_3)Cl_5$	299	1022	61	1.72
	196	1425		
	77	2702		
$(QuH)_2Nb(OC_2H_5)Cl_5$	298	1147	19	1.72
	196	1690		
	77	3664		
$(QuH)_2Nb(O(i\text{-}C_3H_7))Cl_5$	296	1212	20	1.74
	196	1785		
	77	3616		

The C–H stretch of the quinolinium compounds shows a shift from 3400 cm.$^{-1}$ (as in QuHCl and $(QuH)_2CoCl_4$) to 3000 cm.$^{-1}$, which suggests some unusual interaction which weakens the C–H bond.

Reflectance spectra in the visible region were taken for a number of the compounds. The simple alkylammonium salts showed a single (very slightly assymetric) band at 19,600 cm.$^{-1}$ (510 mμ), such as might be expected for an octahedral d^1 complex. Spectra of the pyridinium and quinolinium compounds are much more complex; although no high intensity bands, such as might be associated with charge transfer, are found.

Figure 1 shows the reflectance spectra of four of the pentachloroethoxoniobates and illustrates the dependence of color on the nature of the cation.

The spectra, then, show evidence of interaction of the aromatic cations with the complex, but infrared spectra show that they all retain the N–H bond and so are not directly coördinated through nitrogen to the niobium. The interaction results in a weakening of ring C–H bonds.

The decrease in C–O frequencies may similarly mean the interaction is weakening the alkoxo C–O bond as well.

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(12) D. C. Bradley, F. M. Abd-el Halim, E. A. Sadek, and W. Wardlaw, *J. Chem. Soc.*, 2032 (1952).

The increasing complexity, without a great increase in intensity, in the visible region seems to argue that the nearly octahedral symmetry of the alkylammonium pentachloroalkoxoniobates is greatly reduced (perhaps changed to a strongly tetragonal configuration in which the $^2T_{2g}$ ground state is split to $B_2 + E$ and the ^2Eg excited state to $A_1 + B_1$, thus giving rise, in the extreme cases, to three observable transitions.

That is, the available evidence suggests that the aromatic "-inium" ions interact with the complex, possibly with the alkoxo-group oxygen, and distort the complex further toward tetragonality as well as producing the effects observed for ring C–H and alkoxo C–O stretching frequencies. It is not clear why the pyridinium and quinolinium compounds should show the same C–O frequencies.

It is also possible that the transition $b_2 \rightarrow e$ is at considerably lower energies and would appear in the near-infrared. Unfortunately we are unable to extend the reflectance measurements into that region with present equipment. In $MoOCl_5^{2-}$ that transition is reported to occur at 13,800 cm.$^{-1}$ and so might be expected at still lower frequencies in the $Nb(OR)Cl_5^-$ complexes.[13] Then the absorptions seen at about 20,000 cm.$^{-1}$ would correspond to $b_2 \rightarrow b_1$. If the latter is indeed the case, it is difficult to explain the bands in the aromatic "-inium" compounds and especially in the quinolinium case.

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A Kinetic Study of the Dissociation of Some Arsenic(V) Complexes

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The rates and equilibrium constants for ligand dissociation have been determined for five arsenic(V) complexes with *o*-dihydroxyphenols. These complexes undergo a reversible hydrolytic splitting *via* the reactions

$$[(RO_2)_2As(ORO)(H_2O)]^- + H_3O^+ = H_2O + [(RO_2)_2As(OROH)(H_2O)]$$
$$[(RO_2)_2As(OROH)(H_2O)] = (RO_2)_2AsOH + R(OH)_2$$

An examination of the effect of substituents on R on the rate shows that electron releasing groups facilitate the reaction. The general character of the reaction parameters indicates that the attack of a proton on the anion of the complex leads to the rate determining step and the entropies of activation are consistent with such a charge neutralization step. By carrying out pH titrations on these complexes in times short in comparison with the reaction times, the pK_a values of the parent acids were determined.

The kinetic studies which have been carried out on complexes of the non-transition elements are few in number.[1] The present work is a continuation and extension of previous studies on the hydrolysis or arsenic(V) complexes.[2] Its goal was the elucidation of details of the mechanism of the hydrolysis of arsenic(V) complexes with 1,2-dihydroxy aromatic phenols.

The complexes used in this study were those of arsenic acid with the dihydroxy aromatic phenols: catechol, 3-methylcatechol, 4-methylcatechol, 4-chlorocatechol, and pyrogallol (3-hydroxycatechol). The catechol complex was first prepared by Weinland and Heinzler,[3] and subsequently studied by others.[2,4–6] The 3-methylcatechol, 4-chlorocatechol, and 4-methylcatechol complexes were described in an earlier paper.[7] The pyrogallol complex was prepared in the course of this work.

The structure of these complexes has been the subject of some controversy. Reihlen, Sapper, and Kall[4] studied the catechol compound and assigned to it structure I, Fig. 1, in which two catechol molecules are chelated, one is monodentate, and the sixth coördination position is occupied by H_2O. This was based primarily on the fact that dehydration can remove only four molecules of water from the pentahydrate. Rosenheim and Plato[5] proposed structure II, Fig. 1, in which all three of the catechol molecules were chelated, although they were never able to remove more than four molecules of water without causing decomposition of the complex. We have shown earlier[7] that the corresponding 2,3-dihydroxynaphthalene complex of arsenic(V) exists as a white sesquihydrate and a tan monohydrate. The color change is reversible. The white

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[1] The literature is summarized in R. G. Pearson, D. N. Edgington, and F. Basolo, *J. Am. Chem. Soc.*, **84**, 3233 (1962).

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[7] T. H. Larkins and M. M. Jones, *Inorg. Chem.*, **2**, 142 (1963).