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A Study by Raman Spectroscopy of Complex Ions Formed by Tantalum(V) in the System Ta(V)-HF-NH_4F-H_2O[1]

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The TaF_6^- and TaF_7^{2-} ions formed by tantalum in hydrofluoric acid solutions were identified by comparing the Raman spectra of the solutions with spectra of crystalline $CsTaF_6$ and K_2TaF_7. The Raman spectra of crystalline Na_3TaF_8, $(NH_4)_3TaOF_6$, K_3NbOF_6, and $(NH_4)_3NbOF_6$ were also recorded. Tantalum metal was dissolved in hydrofluoric acid to form solutions $\sim$1 *M* in tantalum and 24, 11, 3.1, and $\sim$0.5 *M* in HF. In 24 *M* HF the TaF_6^- ion is the predominant species with the TaF_7^{2-} ion barely detectable. In 11 and 3.1 *M* HF both TaF_6^- and TaF_7^{2-} ions are present in large amounts. In $\sim$0.5 *M* HF the TaF_6^- and TaF_7^{2-} ions are joined by a third unidentified species which has a Raman line between the lines due to the symmetrical stretches of the two identified species. Ammonium fluoride crystals were added to the solutions in increments, and the variation in the concentrations of the TaF_6^- and TaF_7^{2-} ions was determined by the variation in intensity of their symmetrical stretch vibrations. In $\sim$0 *M* HF at 5.42 *M* NH_4F, the TaF_7^{2-} ion was found to be the predominant species, and the TaF_6^- ion was not present. A new line appeared, however, in the tantalum–oxygen stretch region that is probably due to the $TaOF_6^{3-}$ or $TaOF_5^{2-}$ ion. The TaF_8^{3-} ion was not detected in any of the solutions.

Introduction

Our knowledge of the oxyfluoro and fluoro compounds formed by tantalum and niobium is based mostly on studies of the crystalline compounds. An important extension in our knowledge of the comparative chemistry of these two elements can therefore be made by identifying the species they form under similar conditions in hydrofluoric acid solutions. The method for identifying the species consists of comparing the Raman lines characteristic of known complex ions in crystals with aqueous solutions containing unknown complex ions. This paper extends earlier niobium work[2] to tantalum.

In the case of tantalum, the well-verified fluoride and oxyfluoride complexes made in the past are present in $CsTaF_6$, K_2TaF_7, Na_3TaF_8, and $(NH_4)_3TaOF_6$. We prepared these crystals and took their Raman spectra. Solutions about 1 *M* in tantalum were made up in hydrofluoric acid solution so that the final HF concentrations were 24, 11, 3.1, and $\sim$0.5 *M*. The Raman spectra of these solutions were compared to those of the crystals. The fluoride ion concentration was then varied by addition of ammonium fluoride in order to study the changes in the spectra as a function of fluoride ion concentration.

Experimental Section

Raman spectra were obtained with a Cary Model 81 spectrophotometer. The 4358-A mercury line was isolated with a filter solution of Cyasorb U.V. 24[3] and ethyl violet in *n*-propyl alcohol solution. The lamp current was 13.5 amp.

The cells used to obtain the powder spectra were similar to the one pictured by Busey and Keller.[4] The Kel-F cell with sapphire end window used for the HF solution spectra was the same one used in the niobium study.[2]

Analyses.—Tantalum and niobium analyses were carried out by Davis[5] according to the procedure of Balke.[6] Sodium, potassium, and cesium analyses were done by Feldman[5] using a grating flame photometer. Two methods were used as indicated in the text for the determination of fluoride. Brady[5] determined fluoride by a Willard-Winter distillation from perchloric acid solution followed by a titration with thorium nitrate solution with alizarin red S (sodium alizarinsulfonate) as the indicator. Davis determined fluoride by pyrolysis with moist oxygen at 1000° using a fused and ground Na_2WO_4-WO_3 mixture as the catalyst. The resulting fluoride was titrated with standard base. The ammonium ion was determined by Brady by distillation from caustic solution and titrating with standard acid. The X-ray powder patterns were taken by Sherman.[5]

Materials.—The tantalum metal used in the preparations of crystals and solutions was a minimum of 99.9% pure according to ORNL stores specifications. The niobium powder used in the preparation of $(NH_4)_3NbOF_6$ was from Fisher Scientific Co. K_2TaF_7 was of reagent grade from the Kawecki Chemical Co. All of the other chemicals used in preparing the crystals and solutions were reagent grade.

For the preparation of hydrous tantalum oxide, tantalum metal was dissolved in a hydrofluoric acid–nitric acid mixture, precipitated as the oxide with ammonium hydroxide, redissolved in HF, and reprecipitated as the oxide. The Ta_2O_5 was washed until the wash water was neutral. This oxide was used for the preparation of $CsTaF_6$ according to the procedure of Balke.[6] *Anal.* Calcd for $CsTaF_6$: Cs, 31.1; Ta, 42.3; F, 26.6. Found: Cs, 30.7; Ta, 41.5; F, 26.5 (pyrolysis). The powder pattern of the $CsTaF_6$ was closely similar to that of $CsUF_6$.[7]

The procedure used for the preparation of Na_3TaF_8 is also given by Balke.[6] Platinum metal was used as the catalyst to dissolve tantalum metal in hydrofluoric acid (0.6 mg of Pt dissolved/100 g of Ta). The Na_3TaF_8 was recrystallized from 1% HF. *Anal.* Calcd for Na_3TaF_8: Na, 17.2; Ta, 45.0; F, 37.8. Found: Na, 16.2; Ta, 44.3; F, 37.7 (pyrolysis), 37.0 (Willard–Winter). The X-ray powder pattern to be expected for Na_3TaF_8 was calculated from the single-crystal data of Hoard, Martin, Smith, and Whitney[8] using the computer program of Smith.[9] The observed lines checked with the computed *d* values and intensities.

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[1] Presented at the 16th Annual Southeastern Regional Meeting of the American Chemical Society at Charleston, W. Va., Oct. 15–17, 1964. Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] O. L. Keller, Jr., *Inorg. Chem.*, **2**, 783 (1963).

[3] American Cyanamid Co.

[4] R. H. Busey and O. L. Keller, Jr., *J. Chem. Phys.*, **41**, 215 (1964).

[5] ORNL Analytical Chemistry Division.

[6] C. W. Balke, *J. Am. Chem. Soc.*, **27**, 1140 (1905).

[7] R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.*, **3**, 126 (1964).

[8] J. L. Hoard, W. J. Martin, M. E. Smith, and J. F. Whitney, *J. Am Chem. Soc.*, **76**, 3820 (1954).

[9] D. K. Smith, "A Fortran Program for Calculating X-ray Powder Diffraction Patterns," University of California, Lawrence Radiation Laboratory, UCRL-7196.

The procedure of Joly[10] was used to prepare $(NH_4)_3TaOF_6$. Hydrous tantalum oxide was dissolved in a small excess of hydrofluoric acid. NH_4OH was added with stirring until a white cloud of precipitate formed. An excess of ammonium fluoride was added to bring the white precipitate back into solution. On cooling, crystals of $(NH_4)_3TaOF_6$ formed. *Anal.* Calcd for $(NH_4)_3TaOF_6$: NH_4^+, 14.8; Ta, 49.6; F, 31.2. Found: NH_4^+, 14.8; Ta, 47.6; F, 31.7 (pyrolysis). The X-ray powder pattern showed the *d* values and relative intensities given by Baker and Haendler.[11]

The procedure used for preparing $(NH_4)_3NbOF_6$ was similar to that used for preparing $(NH_4)_3TaOF_6$, except that niobium metal was used as the starting material rather than the oxide. Hydrogen peroxide was used to bring the metal into solution in hydrofluoric acid. Since only a small amount of material was available, the powder pattern and analyses were done on crystals which had been used to obtain the Raman spectrum. Therefore a small amount of impurity was present (see Results and Discussion). *Anal.* Calcd for $(NH_4)_3NbOF_6$: NH_4^+, 19.5; Nb, 33.5; F, 41.2. Found: NH_4^+, 19.2; Nb, 32.4; F, 39.8 (pyrolysis). The X-ray powder pattern showed the main substance present to be $(NH_4)_3NbOF_6$, checking the *d* values and intensities of Baker and Haendler.[11] A few extra weak lines were present, however, as would be expected from the Raman results.

Balke's procedure[6] was modified to prepare K_3NbOF_6. Potassium fluoride crystals were added to a solution of $K_2NbOF_5 \cdot H_2O$ in hot distilled water, and the crystals were brought into solution by adding more water. The mole ratio of K to Nb was 10:1 rather than Balke's 4:1. On cooling, crystals of K_3NbOF_6 formed. The crystals used for the powder pattern and analyses had not previously been used to obtain the Raman spectrum since an unidentified impurity is induced during this process (see Results and Discussion). *Anal.* Calcd for K_3NbOF_6: K, 34.5; Nb, 27.3; F, 33.5. Found: K, 33.6;; Nb, 26.9; F, 32.9 (pyrolysis). The diffraction pattern checked the *d* values and intensities of Williams and Hoard.[12]

Solutions for the Raman spectroscopy were made by dissolving tantalum metal in hydrofluoric acid using platinum foil as the catalyst. The amount of Pt which dissolved was negligible in each case, averaging 0.3 mg of Pt/100 g of Ta. The fluoride content of these solutions was determined by a Willard–Winter distillation. Ammonium fluoride was then added to each solution in increments. If no crystals separated from the solution, its total fluoride concentration was calculated by adding the fluoride from the NH_4F to that already present from the HF and dividing by the total volume of the solution. The NH_4F added was determined by analyzing for NH_4^+ (see Analyses section). In solutions which yielded crystals on the addition of NH_4F, the fluoride concentration in the supernatant liquid was determined by a Willard–Winter distillation. A pure phase separated from solutions 10-F, -G, and -H (Table II). The X-ray powder patterns showed all three of the solutions yielded the same compound. Analysis showed the crystals to be $(NH_4)_2TaF_7$. *Anal.* Calcd for $(NH_4)_2TaF_7$: NH_4^+, 10.3; Ta, 51.7; F, 38.0. Found: NH_4^+, 10.5; Ta, 50.8; F, 36.5 (Willard–Winter). The crystals which separated from other solutions were mixtures.

Dust was removed from all but the solutions most concentrated in ammonium fluoride by passing them through a Millipore cellulosic filter with a pore size of 4500 A. The other solutions were passed through No. 2 filter paper.

Intensities.—The intensities were measured relative to standard solutions of ammonium perchlorate in water. The standard solutions, contained in sealed 19-mm diameter glass cells, were 0.74 and 0.35 *M*. The incident light was not polarized since the depolarization by the Kel-F cell wall and the loss in intensity did not appear to justify this refinement. The areas under the peaks were measured with a planimeter. Of the 25 solutions we studied, seven contained only the TaF_7^{2-} ion. These seven solutions, of widely varying composition, were used to determine the molar intensity of the $\sim$645-cm^{-1} symmetrical stretch of the TaF_7^{2-} ion in arbitrary units. The intensities in arbitrary intensity units per mole of TaF_7^{2-} were for the following solutions (see Table II): 10-I = 1.99; 10-J = 1.95; 12-C = 2.05; 12-D = 2.07; 12-E = 2.09; 13-C = 2.20; 13-D = 2.28. These results are given to show that the total spread was about 14%, and the spread in a given solution series was a few per cent. We can therefore use the appropriate molar intensity for each series to derive the molarity of TaF_7^{2-} in solutions in that series which also contains the TaF_6^- ion. No solution was found which contained only the TaF_6^- ion. Since some of the series 10 solutions were mostly TaF_6^- with only a small peak due to TaF_7^{2-}, an average value of the intensity units per mole of TaF_6^- was derived for that series from three solutions and used to calculate the TaF_6^- concentration in the other seven solutions. Since the TaF_6^- and TaF_7^{2-} peaks were both large in solutions 10-C, 10-D, and 10-E, the molar intensity of TaF_6^- was obtained for those solutions. The measured TaF_7^{2-} concentration was subtracted from the total tantalum to give the TaF_6^- concentration. This concentration was then divided into the measured area under the TaF_6^- symmetrical stretch at $\sim$695 cm^{-1} to give the intensity per mole. The values obtained were 10-C = 1.75, 10-D = 1.80, and 10-E = 1.83. For solutions 12-A, 12-B, 13-A, and 13-B, the TaF_7^{2-} concentration was measured, and the TaF_6^- concentration was obtained by subtracting this value from the total tantalum. The molar intensities of TaF_6^- obtained by dividing these concentrations into the measured areas were 12-A = 2.23, 12-B = 2.38, 13-A = 2.30, 13-B = 2.43.

Results and Discussion

Table I presents the Raman spectra of the four crystalline compounds containing well-characterized complex fluoro and oxyfluoro ions of tantalum. Hoard and co-workers[8, 13] have established the presence of the TaF_7^{2-} and TaF_8^{3-} ions in K_2TaF_7 and Na_3TaF_8. Williams and Hoard[12] have shown that the $NbOF_6^{3-}$ ion is present in K_3NbOF_6. A comparison of the Raman spectrum of $(NH_4)_3NbOF_6$ with that of K_3NbOF_6 (Figure 1) shows that the ammonium salt also contains the $NbOF_6^{3-}$ ion. The *d* values and intensities of the lines in the powder pattern of $(NH_4)_3TaOF_6$ are so close

TABLE I

RAMAN SPECTRA OF CRYSTALS

Compd	Δ cm^{-1} from 4358-A Hg line[a]
$CsTaF_6$ (scanned to 4000 cm^{-1})	272 (m), $\nu_5(F_{2g})$; 581 (w), $\nu_2(E_g)$; 692 (s), $\nu_1(A_{1g})$
K_2TaF_7 (scanned to 4500 cm^{-1})	275 (w); 392 (m); 640 (s)
Na_3TaF_8 (scanned to 2300 cm^{-1})	371 (m); 411 (w); 461 (vw); 614 (s)
$(NH_4)_3TaOF_6$ (scanned to 4000 cm^{-1})	305 (m); 540 (w); 862 (s); 1442 (vw, br);[b] 1703 (w, br);[b] 3150 (s, br)[b]
$(NH_4)_3NbOF_6$[c] (scanned to 4500 cm^{-1})	288 (wm); 537 (wm); 910 (s); 1700 (w);[b] $\sim$3140 (m, br)[b]
K_3NbOF_6[c] (scanned to 3660 cm^{-1})	295 (ms); $\sim$335 (sh); 419 (w, br); 539 (mw); 908 (s)

[a] (vw), very weak; (w), weak; (m) medium; (s), strong; (br), broad; (sh), shoulder. [b] Lines due to NH_4^+. [c] A line appeared very weakly at 860 cm^{-1} after the first scan of the spectrum (see text).

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(12) M. B. Williams and J. L. Hoard, *J. Am. Chem. Soc.*, **64**, 1139 (1942).

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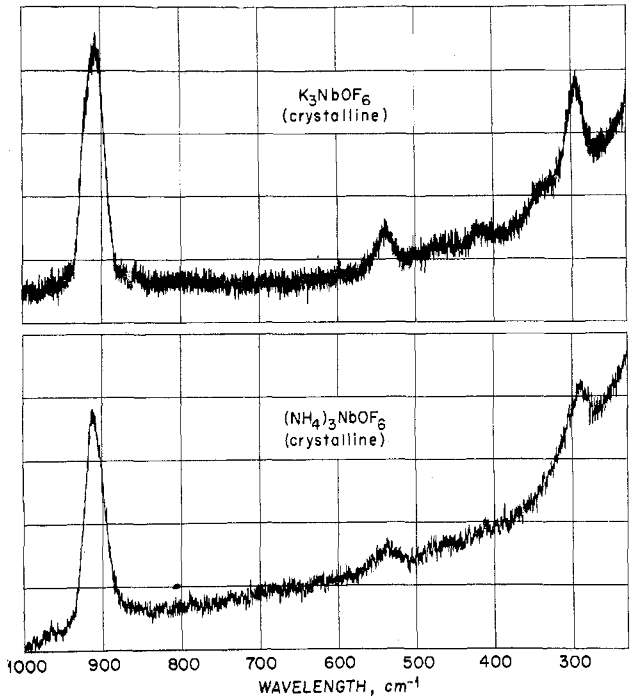

Figure 1.—Raman spectra of K_3NbOF_6 and $(NH_4)_3NbOF_6$ powders. Both spectra run double slit 10 cm × 10 cm^{-1} with a 2-sec period. Scan for K_3NbOF_6, 0.25 cm^{-1}/sec; for $(NH_4)_3NbOF_6$, 0.5 cm^{-1}/sec.

to those in $(NH_4)_3NbOF_6$[11] that the $TaOF_6^{3-}$ ion must be present in the former compound.

In the case of both $(NH_4)_3NbOF_6$ and K_3NbOF_6 a Raman line appeared very weakly at 860 cm^{-1} after the spectrum had been scanned once in the Raman spectrometer. Since this line did not appear in either case in the first spectrum taken, it is attributed to an impurity developed while the spectra are being taken. It was established by Feldman[5] that the tantalum content of the $(NH_4)_3NbOF_6$ was below the limits of detection (0.1%) of his emission spectrograph. Therefore, this line at 860 cm^{-1} could not arise from the $TaOF_6^{-3}$ ion.

The formula of $CsTaF_6$ established by chemical analysis suggests that these crystals contain TaF_6^- ions. The TaF_6^- ion would be expected to have the form of a regular octahedron of symmetry O_h. In the notation of Herzberg,[14] the Raman-active vibrations are ν_1 (A_{1g}), $\nu_2(E_g)$, and $\nu_5(F_{2g})$. The observed spectrum of TaF_6^- is similar to the isoelectronic WF_6,[15] which shows three frequencies in its Raman spectrum: ν_1 772, ν_2 672, and ν_5 316 cm^{-1}. Since W has an atomic number one higher than Ta, the WF_6 frequencies are expected to be higher. The relative intensities of the three lines in the TaF_6^- spectrum are as expected for symmetry O_h. Furthermore, Hoard and Stroupe[16a] found their powder diffraction data to be fully consistent with the assignment of $CsTaF_6$ to the $BaSiF_6$ structural type.[16b] They obtained good agreement between calculated and observed intensities assuming a regular octahedral form for TaF_6^-. The evidence is therefore convincing that a TaF_6^- ion, of at least nearly regular octahedral structure, is present in $CsTaF_6$.

The crystal spectra in Table I give information on the uniqueness of the Raman spectrum of a given tantalum fluoro complex. This is an important point since we have not made all imaginable tantalum fluoro complexes in the crystal form to compare to our solutions. The first three complex ions in Table I differ in the simplest possible way since one fluorine atom is added at a time. These spectra are quite distinct. The symmetrical stretch shifts 52 cm^{-1} in going from TaF_6^- to TaF_7^{2-}, and the middle line shifts 189 cm^{-1}. In the TaF_8^{3-} spectrum, two lines appear at 461 and 411 cm^{-1} which have no counterparts in the TaF_7^{2-} and TaF_6^- spectra, and the symmetrical stretch is 78 cm^{-1} away from that of TaF_6^- and 26 cm^{-1} away from TaF_7^{2-}. The line around 272 cm^{-1} of medium intensity in TaF_6^- and of weak intensity in TaF_7^{2-} has apparently disappeared in TaF_8^{3-}. These three spectra are therefore readily distinguished one from another, and the small shifts we see in solution due to changing the environment cannot confuse them. Since this is so, we assume other possible ions would also have distinct spectra.

The spectra of $(NH_4)_3NbOF_6$, K_3NbOF_6, $K_2NbOF_5 \cdot H_2O$, and $(NH_4)_3TaOF_6$ each show a very strong Raman line in the 900-cm^{-1} range. We follow the rule[17] that totally symmetric vibrations give rise to the strongest Raman lines in assigning this line in the 900-cm^{-1} range as a symmetric stretch vibration. Since these lines occur in the region expected for metal–oxygen stretches,[18] we refer to them as Ta–O and Nb–O stretches. The symmetrical stretches of the tantalum and niobium fluorides occur between 600 and 700 cm^{-1}. Fluoro complexes can therefore be distinguished readily from the above types of oxyfluoro complexes in our solutions.

In their study of pertechnetate, perrhenate, tungstate, and molybdate ions, Busey and Keller[4] found the Raman spectra of the crystalline compounds had to be interpreted in terms of the site symmetry of the ion rather than its molecular symmetry. In this work, on the contrary, we find the spectra of crystalline tantalum and niobium fluorides and oxyfluorides to be closely comparable to their solution spectra with no detectable splitting of the degenerate vibrations. Evidently, the forces which hold these ions together are very much stronger than the forces exerted on them due to their presence in the crystal.

The spectra of the solutions along with their compositions are presented in Table II. The errors in the intensity measurements are probably mostly due to the inaccuracy in choosing the background level. The error listed was obtained by adding the spectroscopically measured molarities of TaF_6^- and TaF_7^{2-} together, noting the difference from the Ta molarity obtained by

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TABLE II

TANTALUM IN AQUEOUS HF–NH_4F SOLUTIONS

Solution	Concentration by analysis (moles/liter)			Concentration from Intensities (moles/liter)		HF (calc.) (moles/liter)	Raman frequency[a] (Δ cm.$^{-1}$ from 4358 Å. Hg)								
	Ta	NH_4^+	F^-	TaF_6^- [error]	TaF_7^{2-} [error]		Ta-O Stretch	TaF_6^-	Ta-F Stretch	TaF_7^{2-}	TaF_6^-	Solvent		TaF_7^{2-}	TaF_6^- and TaF_7^{2-}
10-A	1.03	Zero	29.3	0.85 [5% (−)]	0.09 [50% (−)]	24		697 (s)		650 (vw)					283 (m)
10-B	1.01	0.978	29.6	0.89 [6% (+)]	0.23 [24% (+)]	22		697 (s)		650 (w)					280 (m)
10-C	0.977	1.88	29.7	0.66	0.32	22		698 (s)		650 (mw)					281 (m)
10-D	0.956	2.80	30.0	0.49	0.46	21		697 (ms)		650 (m)					280 (m)
10-E	0.932	3.72	30.2	0.34	0.59	20		696 (s)		649 (s)					280 (m)
10-F	0.778	4.36	27.8	0.18 [8% (−)]	0.57 [2% (−)]	18		696 (m)		647 (s)				378 (w)	280 (mw)
10-G	0.598	4.97	29.3	0.12 [30% (+)]	0.55 [7% (+)]	20		694 (mw)		645 (s)		550 (vw, br)		380 (w)	280 (w)
10-H	0.544	5.76	30.2	0.06 [45% (+)]	0.54 [5% (+)]	20		696 (w)		648 (vs)		550 (vw, br)		380 (w)	278 (vw)
10-I	0.502	7.32	30.6	Zero	0.502	20				647 (vs)		560 (vw, br)		381 (w)	282 (sh)
10-J	0.502	9.37	27.7	Zero	0.502	15				646 (vs)		570 (w)		382 (w)	280 (sh)
12-A	1.03	Zero	17.8	0.53	0.50	11		697 (vs)		648 (s)				384 (vw)	282 (s)
12-B	0.939	2.73	19.1	0.08	0.86	10		695 (w)		646 (s)				377 (w)	280 (vw)
12-C	0.891	4.52	19.9	Zero	0.891	9.2				645 (s)		550 (w, br)		374 (w)	280 (w)
12-D	0.815	6.88	21.1	Zero	0.815	8.5				647 (s)		550 (w, br)		375 (w)	281 (vw)
12-E	0.722	9.06	19.9	Zero	0.722	5.7				645 (s)		570 (m)	440 (w)	375 (wm)	280 (sh)
13-A	1.04	Zero	9.87	0.46	0.58	3.1		696 (vs)		647 (s)	585 (w, br)			370 (vw, br)	279 (m)
13-B	0.976	1.94	11.3	0.09	0.89	2.6		693 (w)		643 (s)		540 (w, br)		375 (w, br)	275 (sh)
13-C	0.922	3.84	12.5	Zero	0.922	2.2				645 (s)		550 (w, br)		377 (w, br)	275 (sh)
13-D	0.820	6.85	14.6	Zero	0.820	2.0				645 (s)		550 (vw, br)		375 (w, br)	278 (sh)
13-E	0.304	11.1	16.1	Zero	0.304	2.9				645 (ms)					
11-A	1.01	Zero	6.63			b		696 (s)	673 (m)	647 (m)	579 (vw, br)				275 (s)
11-B	0.980	0.996	7.42					695 (m)	674 (sh)	647 (s)				376 (vw)	278 (mw)
11-C	0.945	1.90	8.10					695 (vw)		646 (s)				375 (w)	275 (w)
11-D	0.847	5.42	11.0				878 (vw)			642 (s)		535 (w, br)	430 (vw, br)	375 (w)	276 (sh)
11-E	0.473	9.09	12.9				885 (wm)			646 (ms)				375 (vw)	

[a] (vw), very weak; (w), weak; (wm), weak-medium; (mw), medium-weak; (m), medium; (ms), medium-strong; (s), strong; (vs), very strong; (sh), shoulder; (br), broad. [b] HF approximately 0 to 0.5 *M* in series 11 solutions. [c] Solutions 12-A, 13-A, and 11-A scanned to 2200, 2000, and 2050 cm^{-1}, respectively. Water line seen 1645 (m) cm^{-1}. 12-C scanned to 2340 cm^{-1}. NH_4^+ lines seen 1440 (w) and 1700 (w) cm^{-1} and H_2O line 1660 (w) cm^{-1}. 11-D scanned to 3530 cm^{-1}. NH_4^+ lines seen 1445 (w, br) and 1710 (mw, br) cm^{-1} and H_2O lines 1640 (sh) and 3445 (s, br) cm^{-1}. All other solutions scanned to 1000 cm^{-1}.

analysis, and assigning half this difference to each of the two ions. The sign is added to show whether the spectroscopically measured molarity is presumably too low (−) or too high (+). The error in the case of solutions 10-C, -D, and -E (in which both TaF_6^- and TaF_7^{2-} are present in large amounts) is small judging from the near equality of the calculated molar intensities of TaF_6^-. Similarly, the error in solutions 12-A and 13-A should be small (see Experimental Section). The HF concentration listed in Table II is the difference between the determined total fluoride and the fluoride assigned to TaF_6^-, TaF_7^{2-}, and NH_4F.

The weak, broad line seen at about 550 cm^{-1} in some of the solutions was determined to be due to NH_4F by taking the spectrum of 8.09 *M* NH_4F in 10.9 *M* HF which showed a broad line centered at 566 cm^{-1}. The weak, broad line seen in two of the solutions at 430 and 440 cm^{-1} is probably due to a librational mode of water.[19]

In order to show how the identification of the ions in solution is carried out, Figure 2 compares the Raman spectra of solutions 12-C and 13-A with K_2TaF_7 and $CsTaF_6$ crystalline. In solution 12-C, the Raman frequencies occur at 645, 374, and 280 cm^{-1} as compared to 640, 392, and 275 cm^{-1} in K_2TaF_7. The relative intensity of the solution line at 280 cm^{-1} is seen to be similar to that of the crystal at 275 cm^{-1}. Since the lines in solution 12-C fit closely in frequency and relative intensity with the lines of TaF_7^{2-} in K_2TaF_7 but do not fit closely with any of our other crystal spectra, we identify the ion in solution 12-C as the TaF_7^{2-} ion.

In solution 13-A we again see the lines at 647, 370, and 279 cm^{-1} which correspond closely to the frequencies seen in K_2TaF_7, but now the relative intensity of the 279-cm^{-1} line corresponds to that of the 272-cm^{-1} line in $CsTaF_6$ crystalline. The other lines which occur at 696 and 585 cm^{-1} correspond to the lines at 692 and 581 cm^{-1} of the TaF_6^- ion in $CsTaF_6$. Again, there is a marked difference between the solution spectrum and the spectra of our other sample crystals. On this basis we identify the new ion in solution 13-A as the TaF_6^- ion.

In the same way, the presence of the TaF_6^- and TaF_7^{2-} ions in the solutions can be inferred from the data in Table II. For example, solution series 10 begins with Ta in 24 *M* HF. Solution 10-A shows the strong line at 697 cm^{-1} and the medium line at 283 cm^{-1} at the frequencies and relative intensity appropriate for the TaF_6^- ion. The line at 650 cm^{-1} we associate with the TaF_7^{2-} ion. As we add NH_4F, the line at 697 cm^{-1} diminishes in intensity until it disappears in solution 10-I, and at the same time the line at 650 cm^{-1} increases in intensity. As the 650-cm^{-1} line increases in intensity, the weaker line at 380 cm^{-1}, which we also associate with TaF_7^{2-}, begins to appear in solution 10-F

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(19) G. E. Walrafen, *J. Chem. Phys.*, **36**, 1035 (1962).

TABLE III

COMPARISON OF NIOBIUM AHD TANTALUM IN HF SOLUTIONS

Niobium[2]				Tantalum			
[HF], *M*	[Nb], *M*	K^+/Nb	Ions detected	[HF], *M*	[Ta], *M*	NH_4^+/Ta	Ions detected
23	0.39	2	NbF_6^- (100%)	22	0.977	1.92	TaF_6^- (67%) TaF_7^{2-} (33%)
11	0.22	2	$NbOF_5^{2-}$ (100%)	10	0.939	2.91	TaF_6^- (8%) TaF_7^{2-} (92%)
5.2	0.34	2	$NbOF_5^{2-}$ (100%)	2.6	0.976	1.99	TaF_6^- (9%) TaF_7^{2-} (91%)
~0	0.34	2	$NbOF_5^{2-}$ (100%)	~0	0.945	2.02	TaF_6^- (trace) TaF_7^{2-} (~100%)

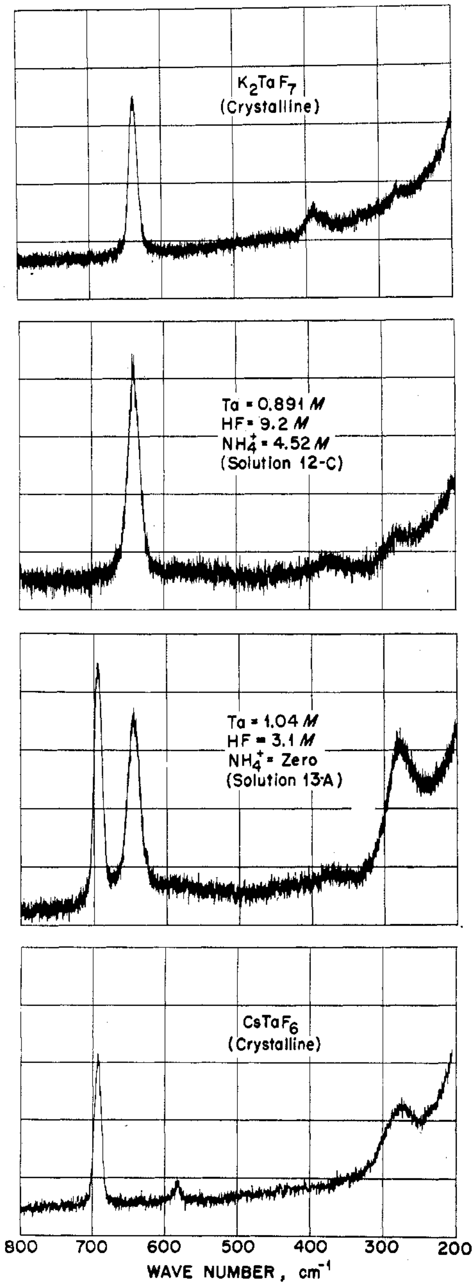

Figure 2.—Comparison of spectra of K_2TaF_7 and $CsTaF_6$ powders with two examples of the system Ta(V)–HF–NH_4F–H_2O. All spectra run double slit 10 cm × 10 cm^{-1} with a 0.5-sec period. K_2TaF_7 scanned at 1 cm^{-1}/sec; all others, 0.5 cm^{-1}/sec.

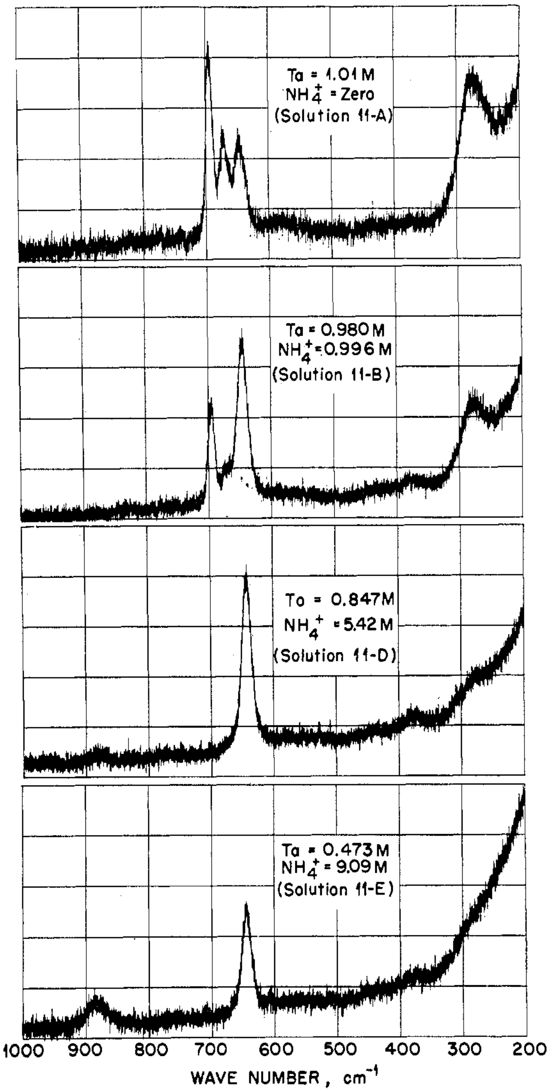

Figure 3.—Raman spectra of Ta(V) in 0 to 0.5 *M* HF with NH_4F concentration as noted. Double slit 10 cm × 10 cm^{-1}; period 0.5 sec; speed 0.5 cm^{-1}/sec.

and becomes quite prominent in the following solutions. Also, the fairly intense line at 280 cm^{-1} gradually loses in intensity until it assumes the relative intensity characteristic of the TaF_7^{2-} ion. So it is clear that, as we add NH_4F to the solutions, TaF_6^- goes over into TaF_7^{2-} ion.

In Figure 3 four of the solutions in about 0 to 0.5 *M* HF are compared. In the top spectrum the three lines due to TaF_6^- are present along with the symmetrical stretch vibration of TaF_7^{2-}. A new line has appeared, however, at 673 cm^{-1} which does not correspond to the spectrum of any of our crystalline compounds. Therefore, we cannot identify this ion. It is likely, however, that it is a fluoro complex rather than an oxyfluoro complex since the line appears in the Ta–F stretch region rather than the Ta–O stretch region. As NH_4F is added, the TaF_6^- ion concentration decreases as the TaF_7^{2-} ion concentration increases and the line at 673 cm^{-1} disappears. In the spectra of solutions 11-D and E a line appears in the tantalum–oxygen stretch region around 880 cm^{-1}. Although this line is most likely due to a $TaOF_6^{3-}$ or $TaOF_5^{2-}$ ion, we cannot identify the ion from this line alone in two solutions.

In Table III a comparison is given of the species tantalum forms under conditions similar to those studied for niobium. It is apparent that the oxyfluoride of niobium is very stable since it is found at high HF concentrations (in fact, $NbOF_5^{2-}$ was detectable in 19 M HF solutions). On the other hand, the oxyfluoride of tantalum disappears at HF concentrations in the 0.1 M range leaving only fluorotantalates. Another notable difference is that all of the tantalum solutions we studied contained the TaF_7^{2-} ion whereas none of the niobium solutions contained the NbF_7^{2-} ion. The niobium study included K:Nb ratios of 2 only, so it may be that higher ratios would lead to formation of NbF_7^{2-}. Indeed, Fordyce and Baum[20] found NbF_7^{2-} to be the predominant species in KF:LiF melts containing Nb(V). Nonetheless, it is clear that tantalum forms the TaF_7^{2-} ion much more readily than niobium forms the NbF_7^{2-} ion.

[20] J. S. Fordyce and R. L. Baum, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 13–17, 1965.

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Infrared and Nuclear Magnetic Resonance Spectra of Hydroxytrimethylplatinum(IV)

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An nmr method for determining the structure of tetrameric hydroxytrimethylplatinum by analyzing the hydroxylic proton resonance is reported. Mixed polymers of hydroxytrimethylplatinum and iodotrimethylplatinum have been detected in the nmr spectra, and interesting changes have been observed in J_{Pt-C-H_3}. Both infrared and nmr evidence for hydrogen bonding of the hydroxylic proton have been obtained. A more complete infrared spectrum is reported in which all of the Pt–O and Pt–C vibration modes are identified. The unsymmetric CH_3 deformation frequency is apparently split by Fermi resonance with an overtone of the Pt–O stretching frequency.

Trimethylplatinum derivatives have been known for many years[1,2] but have still not been fully characterized. Chlorotrimethylplatinum was found to be tetrameric in benzene solution and was shown by single-crystal X-ray analysis[3] to have the structure shown in Figure 1.

Although one can reasonably assume that this structural unit is preserved in solution and that other tetrameric trimethylplatinum derivatives will have a similar structure, a direct determination of the structure in solution seemed most desirable. Proton magnetic resonance of the hydroxy derivative was measured in the hope that the environment of the hydroxylic proton could be determined as well as evaluating the properties of the hydroxyl group in this environment.

Experimental Section

Preparation of Compounds.—Iodotrimethylplatinum was prepared by the method of Foss and Gibson[4] as well as by a modification of this method in which a methyllithium–lithium iodide mixture in diethyl ether was substituted for methylmagnesium iodide. This modification more than doubled the yield (55% based on *cis*-dipyridinetetrachloroplatinum(IV)). The method of Gel'man and Ivanova[2] was also employed with excellent results (66% yield based on sodium hexachloroplatinate). In all syntheses the product was extracted into benzene, dried over sodium sulfate, and recrystallized four times from benzene.

Trimethylplatinum sulfate was prepared by the method of Pope and Peachey.[1]

Hydroxytrimethylplatinum was prepared by adding 0.8 g of freshly precipitated silver hydroxide to 0.2172 g of iodotrimethylplatinum in 50 ml of acetone and 50 ml of benzene. This mixture was refluxed with stirring for 45 hr, then stirred for an additional 11 hr at room temperature. The colorless filtrate yielded a solid which was recrystallized three times to give 0.1258 g of impure hydroxytrimethylplatinum. Integration of the methyl peak intensities in the nmr spectrum indicated a 5% impurity of iodotrimethylplatinum.

A much better synthesis was devised by reaction of ionic, water-soluble trimethylplatinum sulfate to form covalent, water-insoluble hydroxytrimethylplatinum. A 2-ml quantity of a saturated barium hydroxide solution was added to 80.3 mg (0.261 mmole) of trimethylplatinum sulfate dissolved in 3 ml of water. After standing for 24 hr, the mixture was filtered, and the residue was washed with water and acetone (to remove unreacted trimethylplatinum sulfate and barium hydroxide). The remaining residue was boiled in 10 ml of benzene and filtered, and 56.6 mg (0.220 mmole) of hydroxytrimethylplatinum (84%) was crystallized from the filtrate. The sample was analyzed for per cent platinum by thermally decomposing the sample under hydriodic

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[1] W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, **95**, 571 (1909).
[2] O. M. Ivanova and A. D. Gel'man, *Zh. Neorgan. Khim.*, **3**, 1334 (1958).
[3] R. E. Rundle and J. K. Sturdivant, *J. Am. Chem. Soc.*, **69**, 1561 (1947).
[4] M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, 299 (1951).