Table I
Experimental Turbidities, Refractive Index Increments, Solvent Volume Fractions, and pH

M'	$10^5\tau$*	$10^3\Delta n$	Φ	pH
		1:1 Series		
0.19	15.60	5.842	0.947	7.20
0.17	14.12	5.261	0.949	7.20
0.15	12.07	4.592	0.950	7.20
0.13	10.57	3.968	0.950	7.20
0.11	9.17	3.408	0.951	7.14
0.09	7.76	2.776	0.952	7.10
0.07	5.66	2.153	0.952	7.03
0.05	3.99	1.486	0.952	6.96
0.03	2.33	0.871	0.953	6.84
0.01	0.77	0.286	0.953	6.68
		2:1 Series		
0.20	17.36	8.355	0.952	9.96
0.17	14.75	7.076	0.952	9.90
0.14	12.28	5.890	0.952	9.80
0.11	9.52	4.615	0.953	9.75
0.08	7.05	3.319	0.954	9.69

and the points in the concentration range below 0.08 M show a drift to higher values of $1/M_{z'}$. The one additional solution studied, in which Na/V = 1.215, showed a degree of aggregation of 4 also.

The limits of z' for the 2:1 series are 0 and −2, but we have not varied z' to the lower limit, since it was clear that the species has a low charge (magnitude). The degree of aggregation is 2 with a charge of about −0.5. The point for the solution prepared from stock sodium vanadate (1:1) falls on the curve also.

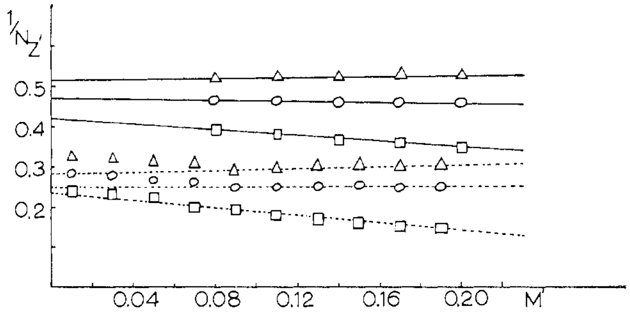

Figure 1.—$1/N_z'$ *vs.* M', solid lines for sodium vanadate (2:1) series, dashed lines for sodium vanadate (1:1) series: △, z' = 0; ○, z' = 0.5; □, z' = 1.0.

By comparison of our pH values with those of Hazel, McNabb, and Santini,[10] we conclude that our solutions are indeed at equilibrium, in sharp contrast to the slow approach to equilibrium we reported recently in the tungstate system.[11]

Acknowledgment.—This work was supported by a grant from the U. S. Army Research Office, Durham, N. C. We wish to thank Dr. D. G. Sharpe of the Biophysics Laboratory of the School of Medicine of the University of North Carolina for the use of a Model 1974 Brice-Phoenix light-scattering photometer.

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Contribution from the Institute for Atomic Research and
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Chemistry of Polynuclear Metal Halides. I. Preparation of the Polynuclear Tantalum Halides Ta_6X_{14}[1a]

By PHYLLIS J. KUHN[1b] and ROBERT E. McCARLEY

Received February 1, 1965

The anhydrous halides $(Ta_6X_{12})X_2$ (X = Br, I) have been produced in good yields by the reduction of the tantalum(V) halides with aluminum foil in a temperature gradient according to the reaction $18TaX_5(g,l) + 16Al(s) = 3(Ta_6X_{12})X_2(s) + 16AlX_3(g,l)$. Final products having atom ratios X/Ta smaller than the calculated 2.33 were shown to contain some tantalum metal. A lower tantalum chloride mixture was prepared by the same procedure, but evidence indicated the principal phase present was $TaCl_{2.5}$ (Ta_6Cl_{15}). However, good yields of the ion $Ta_6Cl_{12}^{2+}$ could be obtained in solution from the anhydrous solids. Reflectance spectra of the anhydrous solids and absorption spectra of aqueous solutions were determined. The spectra were found to exhibit bands very characteristic of the $Ta_6X_{12}^{2+}$ structure.

Introduction

Green aqueous solutions produced by the lower tantalum halides have been attributed by early workers to the presence of species of Ta(II)[2] and Ta(III),[3] Ta_3X_{10},[4] and the ions $Ta_6X_{12}^{2+}$.[5] More recently the existence and structure of the polynuclear ions $Ta_6X_{12}^{2+}$ (as well as $Nb_6X_{12}^{2+}$) in alcohol solutions were ascertained by diffuse scattering of X-rays.[6] However, much of the earlier uncertainty concerning the nature

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(1) (a) Contribution No. 1662. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Presented in part before the Division of Inorganic Chemistry, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964. (b) A portion of a thesis presented by Miss P. J. Kuhn to Iowa State University in partial fulfillment of the requirements for the degree of Master of Science.

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of the species in solution stemmed from incomplete knowledge of the phases present in the anhydrous halides used to prepare such solutions. For example, both $TaCl_2$ and $TaCl_3$ have been reported to produce green aqueous solutions,[3] but convincing evidence that the solid phase had been correctly identified or did not consist of more than one phase was not presented. Similarly, sodium amalgam reduction[5,7] of $TaCl_5$ or $TaBr_5$ at elevated temperature has been used as a method to obtain material from which could be extracted green solutions containing the polynuclear ions, but no information about the anhydrous product was given and yields were poor.

Körösy[8] and Rolsten[9] both obtained green aqueous solutions from lower tantalum iodides. Although the composition of the anhydrous solid corresponded most closely to TaI_3, Körösy emphasized the remarkable similarity of the properties of the aqueous solutions to those of $Ta_6Br_{12}^{2+}$ or $Ta_6Cl_{12}^{2+}$. Rolsten, on the other hand, found a composition close to TaI_4 for a material which he reported to be completely soluble in water with formation of the green color.

Most recently a great deal of progress on the identification of the lower tantalum halide phases has been made. Schäfer and co-workers[10-12] have reported preparation of the compounds $TaCl_{2.5}$, $TaBr_{2.5}$, and $TaI_{2.33}$, which on the basis of preliminary structural data they formulate as the polynuclear halides $(Ta_6Cl_{12})Cl_3$, $(Ta_6Br_{12})Br_3$, and $(Ta_6I_{12})I_2$. McCarley and Boatman[13] have confirmed the existence of $(Ta_6Br_{12})Br_3$ and $(Ta_6I_{12})I_2$ from equilibrium phase studies and in addition established the new phases $(Ta_6Br_{12})Br_2$ and $TaBr_{2.83}$. These studies leave little doubt that these lower halides are actually pure phases containing the polynuclear ion units Ta_6X_{12} in different states of oxidation.

The purpose of this work was to search for a convenient method of preparation of the lower halides $(Ta_6X_{12})X_2$ in good yields. Aluminum reduction of the TaX_5 under conditions reported below was found to be satisfactory for the desired bromide and iodide, but afforded a chloride of somewhat different character.

Experimental

Materials.—Tantalum powder obtained from the Metals Division of the National Research Corp. was used in the preparation of the tantalum(V) halides. Spectrographic analysis showed only a faint trace of niobium to be present in the tantalum. Aluminum foil of *ca.* 99.9% purity was used in the reduction reactions.

Reagent grade halogens were used in the halide preparations. Bromine was dried over P_4O_{10} under vacuum prior to its use. Pure $TaCl_5$, $TaBr_5$, and TaI_5 were prepared by combination of the elements in sealed evacuated tubes at 400°.

Spectra.—Aqueous solution spectra were determined with a Cary Model 14 recording spectrophotometer using 1-cm. quartz cells. For the results reported here solution concentrations were not determined, but were known to be in the range 10^{-4} to 10^{-5} *M*. Reflectance spectra were obtained with a Beckman DU spectrophotometer equipped with the Beckman 2580 reflectance attachment. Magnesium carbonate, used as reference and for dilution of the powdered samples, was dried at 110° *in vacuo* for 12 hr. Dilution ratios were not recorded, but were varied until suitable spectra were obtained. The anhydrous solids were packed into a cavity in a special stainless steel cell in a dry-box and sealed from the atmosphere by covering the solids with a quartz plate which was pressed firmly against a rubber O-ring by a steel retainer. A similar cell contained the reference magnesium carbonate.

X-Ray Data.—Diffraction data were obtained with a 114.59-mm. Debye–Scherrer powder camera. Finely-powdered samples were packed and sealed in 0.2-mm. Lindemann glass capillaries. The samples were exposed to Ni-filtered, Cu Kα radiation for 16–30 hr., depending upon the sample.

The Reduction Method.—In the reactions between aluminum and the tantalum(V) halides described below a sealed tube–temperature gradient technique was always used. The desired temperature gradient was maintained by using a tube furnace which was wound separately along each half of its length. Chromel–alumel thermocouples were strapped with nichrome wire to each end of the reaction tube and were used in conjunction with time-proportioning, on-off controllers to regulate the temperature at each end of the furnace separately to within *ca.* ±2°. A stainless steel liner which fit snugly against the ceramic furnace tube was used to smooth the temperature gradient along the furnace length. In these reactions the furnace was tilted slightly from the horizontal so that the higher temperature was always at the lower end of the reaction tube. In this way the volatile tantalum(V) and aluminum(III) halides condensed at the upper end and flowed back to the reaction zone to maintain a constant reflux action.

Reduction of Tantalum(V) Chloride.—In this reaction aluminum was used to effect reduction of a quantity of $TaCl_5$ in slight excess (*ca.* 1 g.) of that calculated for complete conversion to $(Ta_6Cl_{12})Cl_2$. In a typical reaction 10 g. of $TaCl_5$ and 0.5 g. of aluminum foil were permitted to react in an evacuated, sealed Vycor tube of dimensions 20 mm. o.d. × 30 cm. For convenient loading of the aluminum the foil was first formed into several small rolls, each about 5–6 cm. long. The initial heating in a 400/200° temperature gradient for 1.5 days gave a black product from which $AlCl_3$ and excess $TaCl_5$ were removed by sublimation at 200°. The sublimation was effected simply by removing one end of the tube from the furnace and adjusting the temperature at the end containing the product to 200°. Subsequently the temperature of the reaction product was raised to 550° and maintained for 10 hr. This treatment afforded a product which appeared green when hot but upon cooling turned greenish brown. X-Ray diffraction data for this product indicate the principal phase to be $(Ta_6Cl_{12})Cl_{13}$.[10] Values for the *d* spacings (Å.) having relative intensities (in parentheses) greater than 3 are: 7.26 (10), 3.22 (7), 3.14 (7), 2.77 (8), 2.54 (4), 2.43 (5), 2.40 (4), 2.36 (9), 2.19 (8), 2.14 (8), 2.05 (8), 2.01 (4), 1.996 (4).

Anal. Calcd. for Ta_6Cl_{15}: Ta, 67.12; Cl, 32.88; Cl/Ta, 2.50. Found: Ta, 68.71, 68.53; Cl, 31.14, 30.07; Cl/Ta, 2.27 (average).

A sample of this product dissolved incompletely in water to produce an intense blue-green solution which exhibited absorption maxima at 755, 637, 398, and 329 mμ; a shoulder was observed at *ca.* 470 mμ. The reflectance spectrum of the anhydrous solid showed peaks at 926, 755, 410, and 350 mμ. Spectra of the aqueous solution and anhydrous solid are shown in Figure 1.

Exhaustive extraction of a weighed sample of the solid having a Cl/Ta ratio of 2.27 with hot water left a small amount of a black powdery residue. The soluble fraction constituted 88.0% of the original sample weight. Analysis of the insoluble residue showed Ta, 79.42; Cl, 15.67; Cl/Ta, 1.00. However, an X-ray diffraction pattern of the residue was in substantial agreement

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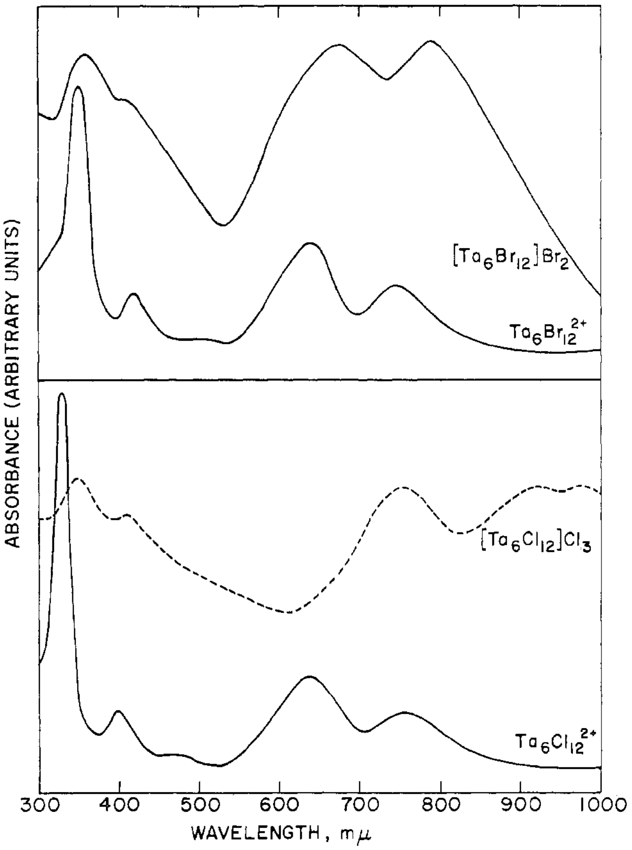

Figure 1.—Reflectance spectra (upper curves) and aqueous solution absorption spectra (lower curves) of the polynuclear tantalum bromide and chloride.

with that of the starting material. Hence the insoluble residue was considered to be a mixture of Ta with some undissolved $(Ta_6Cl_{12})Cl_3$. The presence of a small amount of metal thus was considered to be responsible for the low value 2.27 for Cl/Ta in the anhydrous compound (see under Results and Discussion).

Dodeca-μ-bromo-hexatantalum Dibromide.—Synthesis of the lower tantalum bromide $(Ta_6Br_{12})Br_2$ was analogous to that given above. In this case 6 g. of $TaBr_5$ were added to 0.23 g. of aluminum foil in a Vycor tube, which was subsequently evacuated, sealed, and heated for 2 days in a gradient of 450/280°. The reaction was halted by pulling the tube partially out of the furnace so that $TaBr_5$ and $AlBr_3$ were sublimed from the product at 280°. Subsequently the furnace temperature was increased to 570° for 5 hr. The product thus obtained was a deep green powder.

Anal. Calcd. for Ta_6Br_{14}: Ta, 49.25; Br, 50.75; Br/Ta, 2.33. Found: Ta, 49.61, 50.00; Br, 49.82, 49.53; Br/Ta, 2.26 (average).

Values for the *d* spacings (Å.) and relative intensities of the more intense lines in the X-ray diffraction pattern are: 7.44 (10), 3.51 (4), 2.87 (4), 2.74 (4), 2.42 (10), 2.37 (5), 2.25 (5), 2.19 (5), 2.12 (4), 1.91$_8$ (4), 1.86$_6$ (4).

The product described above dissolved almost completely in water with the formation of an intense green color. An absorption spectrum of the solution showed maxima at 747, 639, 420, and 352 mμ; in concentrated solution a shoulder appeared at *ca.* 495 mμ. The reflectance spectrum of the anhydrous solid showed maxima at 790, 678, 408, and 358 mμ. As shown in Figure 1 the peaks in the reflectance spectrum were broad and not as well-resolved as in the solution spectrum.

Exhaustive extraction of a weighed sample of anhydrous product having the over-all composition $TaBr_{2.12}$ with hot water resulted in dissolution of 95% of the sample. An X-ray diffraction pattern of the gray residue showed only very broad and diffuse lines corresponding roughly to the lines of metallic tantalum. Correction of the composition of $TaBr_{2.12}$ for the weight of metal present gave the composition $TaBr_{2.33}$ (Ta_6Br_{14}) for the water-soluble fraction. Similar evidence indicated that all products having a Br/Ta ratio less than 2.33 contained small amounts of tantalum metal.

Dodeca-μ-iodo-hexatantalum Diiodide.—In a typical preparation 6 g. of TaI_5 and 0.15 g. of aluminum foil were transferred to a Pyrex tube, which was evacuated and sealed. The tube was placed in a furnace under a 475/300° temperature gradient for 2 days. Subsequently the AlI_3 and excess TaI_5 were sublimed from the nonvolatile black product at 300° for 24 hr.

Anal. Calcd. for Ta_6I_{14}: Ta, 37.93; I, 62.07; I/Ta, 2.33. Found: Ta, 37.98, 38.30; I, 61.52, 61.86; I/Ta, 2.31 (average).

Values for the *d* spacings (Å.) and relative intensities of the major lines in the X-ray diffraction pattern are: 8.02 (10), 3.23 (3), 3.14 (8), 2.95 (5), 2.61 (10), 2.37 (3), 2.29 (3), 2.22 (3), 2.09 (3), 2.06 (3), 2.04 (3), 2.01 (4), 1.61$_8$ (5).

This compound dissolved in water to produce intense green solutions very similar in appearance to solutions of the corresponding chloride and bromide. The aqueous solution absorption spectrum exhibited peaks at 750, 635, 460, and 343 mμ; shoulders were observed at *ca.* 390 and 370 mμ. On standing for several days a fading of the color of these solutions was noticed, and a white precipitate of hydrous Ta_2O_5 formed.

Method of Analysis.—For elemental analyses the compounds were found to be increasingly difficult to decompose in the order $(Ta_6I_{12})I_2 < (Ta_6Br_{12})Br_2 < (Ta_6Cl_{12})Cl_3$. The iodide and bromide were hydrolyzed with boiling ammonia solution (several hours) and acidified with dilute nitric acid to precipitate hydrous Ta_2O_5. Tantalum then was determined gravimetricly as Ta_2O_5 and the halogens volumetrically by the Volhard method. In the case of $(Ta_6Cl_{12})Cl_3$ addition of ammonia solution precipitated a relatively stable compound thought to be $Ta_6Cl_{12}(OH)_2$, since on acidification the precipitate dissolved, producing the characteristic green solution. Hence the heated aqueous solutions of the chloride were oxidized by dropwise addition of 6 *N* nitric acid and the elements determined as described above.

Results and Discussion

In each of the synthesis reactions a two-step procedure was used. In the first step the reaction given by eq. 1 was assumed to occur, but care was taken so that a slight excess of TaX_5 over that needed for (1)

$$18TaX_5(g,l) + 16Al(s) = 3Ta_6X_{14}(s) + 16AlX_3(g,l) \quad (1)$$

was always present. This precaution was necessary in order to assure complete removal of aluminum and to minimize formation of tantalum metal. Reactions performed with a slight deficiency of TaX_5 were found to yield final products which sometimes were pyrophoric. The products obtained after the first step usually had X/Ta values considerably above that of $TaX_{2.33}$ (Ta_6X_{14}), the exact composition depending on the amount of excess TaX_5 used in the reaction. The higher X/Ta values indicated some conversion to the higher halides, *e.g.*, TaX_4 or TaX_3.

The second step in the preparation procedure involved a final heat treatment *in vacuo* to remove AlX_3 and unreduced TaX_5 and to decompose the intermediate halides such as TaX_4. Composition data were collected for products obtained as a result of experiments where the temperature of the final heat treatment was varied over the range 300–600°. These data demonstrated that final temperatures above *ca.* 500 and 550° for the $(Ta_6Cl_{12})Cl_3$ and $(Ta_6Br_{12})Br_2$, respectively, are required for elimination of the higher halides from the products at a convenient rate. The temperature of the final heat treatment of the $(Ta_6I_{12})I_2$ is not so critical. Indeed, the data suggest no higher halide is formed in this case and that a temperature (300–400°) sufficient to remove excess TaI_5 is all that is required; this is confirmed in the TaI_5–Ta phase diagram which shows $(Ta_6I_{12})I_2$ to be the only phase below TaI_4.[13]

However, in the preparation of $(Ta_6Cl_{12})Cl_3$ and $(Ta_6Br_{12})Br_2$ use of excessively high temperatures or long heating periods in the final step led to a higher metal content in the products. For best results a temperature near 500° for the chloride and 550° for the bromide should be used. It should be noted that the presence of small amounts of metal in the products is not serious if the product is to be used for preparation of solutions in different solvents. On the other hand, the presence of higher halides could produce unwanted species in solution, either by direct dissolution or by hydrolysis.

Samples of the lower bromide and iodide prepared by prolonged heating in the final heat treatment, reaction with excess aluminum in the initial reaction, or equilibration of final products with tantalum metal gave products having over-all X/Ta ratios from 0 to 2.33. Regardless of the final X/Ta ratio only the X-ray powder patterns of the $(Ta_6X_{12})X_2$ phases were obtained for these products. No changes in the *d* spacings as a function of X/Ta were noted for any of these mixtures. Hence the phases identified as $(Ta_6X_{12})X_2$ appear to be of invariant composition. However, it is peculiar that none of the lines of Ta could be definitely identified in these patterns, even though some very broad and diffuse lines corresponding roughly to those of Ta did appear in patterns of products having very low X/Ta. Also, as described in the Experimental section, after aqueous extraction of the bromide of composition $TaBr_{2.12}$ diffuse lines corresponding to those of Ta were found in the diffraction pattern of the insoluble residue. Our conclusion is that Ta is present in all of the products having a composition lower than $TaX_{2.33}$, but that the metal is extremely finely divided and hence does not yield sharp lines in the diffraction patterns.

In the case of the lower tantalum chloride the X-ray diffraction patterns show only the lines of $(Ta_6Cl_{12})Cl_3$ as reported by Schäfer,[10] even though the Cl/Ta ratios generally were less than 2.5. Initially it was thought that the chloride products were the $(Ta_6Cl_{12})Cl_2$ phase. But an authentic sample of $(Ta_6Cl_{12})Cl_3$ prepared according to the method given by Schäfer[10] gave a powder pattern in close agreement with that given by the product of the aluminum reduction. From the X-ray patterns it also is obvious that $(Ta_6Cl_{12})Cl_3$ and $(Ta_6Br_{12})Br_3$ are isostructural. The latter compound has been obtained *via* transport reactions by Schäfer[14] and also identified in the tantalum–tantalum bromide phase diagram in this laboratory.[13] Thus it appears that $(Ta_6Cl_{12})Cl_3$ is the principal product of the aluminum reduction method described above, but that the Cl/Ta ratios are lowered by the presence of tantalum metal.

Although the product of the chloride reduction may consist principally of $(Ta_6Cl_{12})Cl_3$, on extraction of this product into hot water a solution containing the ion $Ta_6Cl_{12}^{2+}$ is obtained in good yields. The mode of formation of the $Ta_6Cl_{12}^{2+}$ ion from the solid, which must contain the $Ta_6Cl_{12}^{3+}$ ion, is not known. Further work on the solution chemistry of the polynuclear halide ions is in progress. It has been found that the units Ta_6X_{12} can exist in several oxidation states, but in aqueous solution[15] the only states observed are the $Ta_6X_{12}^{2+}$ and $Ta_6X_{12}^{4+}$. It is possible that on passing into solution the $Ta_6Cl_{12}^{3+}$ ion is reduced by water. No evidence has been obtained that disproportionation (with formation of both $Ta_6Cl_{12}^{4+}$ and $Ta_6Cl_{12}^{2+}$) results when the $(Ta_6Cl_{12})Cl_3$ is dissolved.

The X-ray diffraction patterns of $(Ta_6Br_{12})Br_2$ and $(Ta_6I_{12})I_2$ clearly indicate that these compounds are isostructural. Although the phase $(Ta_6Br_{12})Br_3$ also exists,[13] it apparently is not formed in the initial aluminum reduction of $TaBr_5$ or it is decomposed in the final heating of the product at $\geq 550°$. Samples of $(Ta_6Br_{12})Br_2$ dissolved easily and almost completely in cold water to provide directly solutions of $Ta_6Br_{12}^{2+}$ free of other metallic ions. As noted in the Experimental section, solutions of $(Ta_6I_{12})I_2$ are unstable and after a few days decompose completely to give the hydrated Ta_2O_5.

A comparison of the solution and reflectance spectra of the anhydrous compounds is given in Figure 1. Here it is evident that in the case of the bromide the same species $Ta_6Br_{12}^{2+}$ is responsible for the spectrum of both the solid and the solution. In the case of the chloride, however, the reflectance spectrum is not in such good agreement with that of solutions of $Ta_6Cl_{12}^{2+}$ and constitutes further evidence that the absorbing species in the solid is different from that in solution. The black $(Ta_6I_{12})I_2$ did not yield a definitive reflectance spectrum by the experimental technique employed here.

Absorption maxima for the aqueous ions $Ta_6X_{12}^{2+}$ are given in Table I. Particularly noteworthy is the close agreement between the positions of the two lowest energy bands near 15,700 and 13,300 cm.$^{-1}$ in each spectrum. These bands have extinction coefficients[16]

TABLE I

ABSORPTION MAXIMA (CM.$^{-1}$) FOR AQUEOUS $Ta_6X_{12}^{2+}$ SOLUTIONS

$Ta_6Cl_{12}^{2+}$	$Ta_6Br_{12}^{2+}$	$Ta_6I_{12}^{2+}$
30,400	28,410	29,150
25,130	23,810	21,740 (sh)
21,280 (sh)	20,240 (sh)	
15,700	15,650	15,750
13,240	13,390	13,330

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[16] R. E. McCarley and B. G. Hughes, to be published.

in the range (3–6) × 10^3 and appear to be characteristic of the unit Ta_6X_{12} with +2 charge. Because these two bands are independent of the halide they also must be associated with transitions involving only metal orbitals within the octahedral arrangement[6] of metal atoms. The positions of the remaining bands shift to lower energies in the order $Ta_6Cl_{12}^{2+} > Ta_6Br_{12}^{2+} > Ta_6I_{12}^{2+}$. A more detailed account of the spectra, magnetic susceptibilities, and chemical properties of these ions will be given in a subsequent paper.[16]

Contribution from the Institute for Atomic Research and
Department of Chemistry, Iowa State University, Ames, Iowa

The Equilibrium Phase Diagrams for the Tantalum–Tantalum Bromide and Tantalum–Tantalum Iodide Systems[1]

By ROBERT E. McCARLEY and JAMES C. BOATMAN

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The tantalum–tantalum bromide and the essential features of the tantalum–tantalum iodide system have been elucidated. In the bromide system four phases of composition lower than $TaBr_5$ were established, *viz.*, $TaBr_4$, $TaBr_{2.83}$, $TaBr_{2.5}$, and $TaBr_{2.33}$. By comparison the iodide system is very simple as evidenced by only the two lower phases TaI_4 and $TaI_{2.33}$. In the bromide system a eutectic occurs at 267° and the composition $TaBr_{4.87}$. The $TaBr_4$ melts incongruently at 392° to form liquid of composition near $TaBr_{4.85}$ and the next lower solid $TaBr_{2.83}$. Equilibrations of $TaBr_4$ at a series of temperatures above 400° established that $TaBr_{2.83}$ melts incongruently within the interval 447–453° to form bromine-rich liquid and the phase $TaBr_{2.5}$. Similarly it was determined that $TaBr_{2.5}$ melts incongruently to form $TaBr_{2.33}$ in the interval 671–680°. Exact location of the melting temperatures for the bromides with Br/Ta < 4 was hindered by the very sluggish reactions. That $TaBr_{2.33}$ was the lowest phase in the system was established by equilibrations of the higher halides with tantalum at temperatures up to 750°; a melting point for $TaBr_{2.33}$ was not observed. In the iodide system the melting point of TaI_5 occurred at 382°, with a eutectic at 365° and the composition $TaI_{4.87}$. Decomposition of TaI_4 into iodine-rich liquid and $TaI_{2.33}$ occurred in the interval 395–402° at a very low rate. Equilibrations of $TaI_{2.33}$ and Ta up to 815° provided no evidence for any new phases. Both $TaBr_{2.33}$ and $TaI_{2.33}$ provide aqueous solutions of the ions $Ta_6Br_{12}^{2+}$ and $Ta_6I_{12}^{2+}$. Hence these compounds are formulated correctly as $(Ta_6Br_{12})Br_2$ and $(Ta_6I_{12})I_2$. The chemical properties and stoichiometry of the phases $TaBr_{2.5}$ and $TaBr_{2.83}$ suggest that they should be formulated as $(Ta_6Br_{12})Br_3$ and $(Ta_6Br_{12})Br_5$, respectively.

Introduction

In previous work in this laboratory[2] it was found that the polynuclear halides $(Ta_6Br_{12})Br_2$ and $(Ta_6I_{12})I_2$ could be prepared *via* aluminum reduction of the respective tantalum(V) halides. But the question whether or not these compounds were equilibrium compounds in the tantalum–tantalum halide systems was not answered. Other workers have obtained aqueous solutions of the polynuclear tantalum halides *via* reduction of the tantalum(V) halides with sodium,[3] aluminum,[4,5] or lead,[6,7] followed by extraction of the products into water. However, these workers did not successfully identify the anhydrous phase giving rise to these solutions.

More recently Schäfer, *et al.*, have prepared the lower halides $TaCl_3$,[8] $TaCl_{2.5}$,[8] $TaBr_3$,[9] $TaBr_{2.5}$,[9,10] and $TaI_{2.33}$[10] by means of chemical transport reactions. The compounds $TaCl_{2.33}$ and $TaBr_{2.33}$ were not observed in their work.[9] In order to clarify the question about the number of reduced halides in the tantalum–tantalum halide systems this work was undertaken. Because excessive pressures were encountered in sealed tube equilibrations at high temperatures in the tantalum chloride system, a detailed investigation of the tantalum bromide and iodide systems was undertaken first.

Experimental

Materials.—The tantalum(V) halides were prepared by direct combination of the elements at elevated temperatures in sealed, evacuated tubes. Subsequent handling of these and other reactive materials was always done on a high vacuum line or in the glove box. The glove box was filled with argon maintained at a dew point of *ca.* −75°.

Tantalum(IV) Bromide.—After some exploratory work it was found that large amounts of $TaBr_4$ were most conveniently prepared by aluminum reduction of $TaBr_5$ at 250°. In a typical preparation 0.2 g. of aluminum foil and 15 g. of $TaBr_5$ were placed in a Pyrex tube which was *ca.* 35 cm. long with a constriction located about one-third of the distance from the end containing the reaction mixture. The tube was evacuated, sealed, placed in a furnace with the end containing the aluminum foil lowered from the horizontal, and heated to 250°. After 7 days the reaction was complete and a dark crystalline solid was obtained. Excess $TaBr_5$ and product $AlBr_3$ were removed by sublimation at 225° for 16 hr. leaving the desired $TaBr_4$ as residue.

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