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**Kinetics and Mechanism of Oxidation of the Tantalum Halide Cluster Ion  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  by Cobalt(III) Complexes and by Miscellaneous Oxidizing Agents<sup>1</sup>**

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Kinetic studies have been carried out on the reaction of  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  and aminocobalt(III) complexes. Most extensive studies were carried out on the oxidation by *cis*- $\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}^{2+}$ ; the second-order rate constant is  $2.5 \pm 0.2 M^{-1} \text{sec}^{-1}$  at  $34.7^\circ$  and  $\mu = 0.052 M$ . The value of  $k_2$  was independent of the specific anion used to maintain ionic strength and independent also of the charge type of the inert cations present. In a series of experiments at varying ionic strength ( $0.009 \leq \mu \leq 0.052$ ), the value of  $k_2$  followed the relation  $\log k_2 = \log(1.35) + 0.51 \times 4.0 \times \mu^{1/2}$ , consistent with the limiting Brønsted-Debye-Hückel relation. Activation parameters were obtained at  $\mu = 0.05 M$ . No spectral evidence for ion association of  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  and  $\text{Cl}^-$  was obtained over the concentration range  $2 \times 10^{-5} \leq [\text{Cl}^-] \leq 0.1 M$ . In a period of 13 hr, chloride exchange of  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  and  $\text{Cl}^-$  was negligible. Mercury(II), cerium(IV), and copper(II) oxidized  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  to the 3+ cluster with second-order rate constants of 3.46,  $1.5 \times 10^7$ , and  $0.027 M^{-1} \text{sec}^{-1}$ , respectively, at  $25.0^\circ$  in 1.00 *F* perchloric acid. Electron exchange between cluster ions proved to be immeasurably rapid at  $25^\circ$  in 1.0 *F* perchloric acid. For the reportionation reaction of  $(\text{Ta}_6\text{Br}_{12})^{2+}$  and  $(\text{Ta}_6\text{Br}_{12})^{4+}$  we concluded  $k \geq 5 \times 10^7 M^{-1} \text{sec}^{-1}$ , and for the net oxidation of  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  by  $(\text{Ta}_6\text{Br}_{12})^{3+}$   $k \geq 1 \times 10^9 M^{-1} \text{sec}^{-1}$ .

**Introduction**

The mechanisms of electron-transfer reactions involving cluster ions have received relatively little previous study, although similar reactions with iron(III)<sup>2</sup> and vanadium(V)<sup>3</sup> have been reported, as have electron-transfer reactions of polytungstate species.<sup>4</sup> Reactions such as these involve a species rather different from simple first-row metal complexes. It is a question of some interest to learn whether the general ideas of mechanism that have been developed in the latter cases can be extended to the former.

We report here on studies of reactions involving cobalt(III) complexes, cerium(IV), mercury(II), and copper(II). In addition, two types of reactions involving electron transfer between different cluster ions were also studied.

**Experimental Section**

**Materials.**—Solutions of  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  and  $(\text{Ta}_6\text{Br}_{12})^{2+}$  were prepared as before.<sup>3</sup> Solutions of  $(\text{Ta}_6\text{X}_{12})^{4+}$  were prepared by chlorine oxidation, the excess of which was removed in a stream of nitrogen. The 3+ cluster,  $(\text{Ta}_6\text{X}_{12})^{3+}$ , was prepared from equimolar amounts of 2+ and 4+. Solutions of  $(\text{Ta}_6\text{X}_{12})^{2+}$  were analyzed on the basis of the known extinction coefficients at 6370 Å.<sup>3</sup>

The cobalt(III) complexes used were *cis*- $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]\text{SO}_4$ ,  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]\text{Cl}_3$ , *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , and *cis*- $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2]\text{Cl}_3$ . The complexes were prepared according to the directions given in the ref 5 and 6.

Other oxidizing agents were used as their perchlorate salts in acidic solution. Mercury(II) was prepared from the oxide;<sup>7</sup> cerium(IV) and copper(II) were available commercially (G. F.

Smith). Lithium and barium perchlorates were prepared from their carbonates and recrystallized before use. Barium chloride and lanthanum chloride (prepared from the oxide) were also recrystallized. Conductivity water was used in all solutions. Other materials were reagent grade chemicals.

**Procedures.**—Rate measurements were made spectrophotometrically, generally at 6370 Å where  $(\text{Ta}_6\text{X}_{12})^{2+}$  ions have high molar absorptivities. A Cary Model 14 recording spectrophotometer and a Beckman Model DU, the latter modified by a Gilford absorbance converter unit and a potentiometric recorder, were used for most of the reactions studied here. The general procedure has been described previously.<sup>8,9</sup> A few of the more rapid reactions were studied by the stopped-flow technique.<sup>10</sup>

Most of the reactions considered here were studied under conditions where a large excess of oxidizing agent was present. In such cases, precise knowledge of the initial concentration of  $\text{Ta}_6\text{X}_{12}^{2+}$  proved to be immaterial; the values from the spectrum sufficed.<sup>3</sup> Cobalt(III) complexes generally were analyzed spectrophotometrically as Co(II) in 50% acetone solutions containing thiocyanate ion;<sup>11</sup> reduction was accomplished with  $\text{Cr}^{2+}$  or with metallic tin. Most cobalt(III) solutions were analyzed in this fashion, a separate solution and a separate analysis being made for every run. Less frequently, cobalt(III) solutions were analyzed from the molar absorptivity values established from many determinations. Other materials were analyzed by standard procedures based on volumetric or spectrophotometric methods.

**Results**

**Association of  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  and  $\text{Cl}^-$ .**—The cluster ion  $(\text{Ta}_6\text{X}_{12})^{2+}$  may possibly associate with anions; such outer-sphere complexes or ion pairs are known for more conventional complexes of transition metals. Moreover, derivatives containing added KCl are known (e.g.,  $\text{K}_4\text{Ta}_6\text{Cl}_{18}$ ). Such compounds probably contain the  $(\text{Ta}_6\text{X}_{12})\text{X}_4^{4-}$  unit.<sup>12</sup>

It was shown by cation exchange that dilute ( $10^{-5}$ – $10^{-3} M$ ) solutions contained a cationic cluster unit whether prepared from  $\text{Ta}_6\text{Cl}_{14}$  or from the KCl ad-

(1) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; Contribution No. 2204. Based in part on the M.S. thesis of D. J. Boone, Iowa State University, 1967.

(2) J. H. Espenson and R. E. McCarley, *J. Am. Chem. Soc.*, **88**, 1063 (1966).

(3) J. H. Espenson, *Inorg. Chem.*, **7**, 631 (1968).

(4) P. G. Rasmussen and C. H. Brubaker, Jr., *ibid.*, **3**, 977 (1964).

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(6) G. G. Schlessinger, "Inorganic Laboratory Preparation," Vol. 6, McGraw-Hill Book Co., Inc., New York, N. Y., 1963: (a) p 207, (b) p 237, (c) p 214, (d) p 235.

(7) J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **4**, 527 (1965).

(8) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

(9) J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).

(10) D. W. Carlyle and J. H. Espenson, *ibid.*, **6**, 1370 (1967).

(11) E. B. Sandell, "Calorimetric Determination of Traces of Metals," 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1959, p 426.

(12) R. E. McCarley and J. L. Meyer, private communication.

duct. The cluster is also taken up by cation-exchange resin, and not by anion resin, in solutions of either starting material in HCl solution. Spectra of solutions from either source are also identical.

A careful series of measurements was made of the spectrum of  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  in the uv region in a series of solutions of varying  $[\text{Cl}^-]$  at constant  $[\text{H}^+] = 1.0 M$  and unit ionic strength. Measurements covered the range  $2 \times 10^{-5} \leq [\text{Cl}^-] \leq 0.1 M$ ; over that entire range the spectrum showed no observable shifts in wavelengths of maximum or minimum absorption and no detectable changes in intensity. Three interpretations can be made. Either the spectral procedure is not sensitive to such ion-pair formation, or such association was complete at the lowest chloride ion concentration, or association was quite small at the highest concentration. In view of the ion-exchange results cited above, we favor the latter interpretation.

**Cobalt(III) Complexes.**—The most extensive series of kinetics experiments were carried out on the reaction of *cis*- $\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}^{2+}$  with  $(\text{Ta}_6\text{Cl}_{12})^{2+}$ . The stoichiometry of the reaction is given in eq 1.  $\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}^{2+} + (\text{Ta}_6\text{Cl}_{12})^{2+} + 4\text{H}^+ = \text{Co}^{2+} + (\text{Ta}_6\text{Cl}_{12})^{3+} + 4\text{NH}_4^+ + \text{H}_2\text{O} + \text{Cl}^-$  (1)

This result was established by analyzing both the Co(II) and  $(\text{Ta}_6\text{Cl}_{12})^{3+}$  produced in a reaction with excess Co(III) complex. The Co(II) was analyzed spectrophotometrically as the thiocyanate complex, and a qualitative and quantitative analysis for  $(\text{Ta}_6\text{Cl}_{12})^{3+}$  was obtained from its known absorption spectrum at 7000–8200 Å. The concentrations so determined were equal to one another within experimental error, and were also equal to the  $(\text{Ta}_6\text{Cl}_{12})^{2+}$  originally introduced.

Attempts to obtain precise and reproducible kinetic data for reaction 1 were at first unsuccessful. The possibility of metal ion catalysis was investigated by adding  $\sim 10^{-5} M$  aluminum(III) or iron(III) ions, both of which may be present at somewhat lower concentration in the cluster complex. No rate effects were noted. Strict adherence to the preparative details for the cobalt(III) complex, its conversion from the sulfate to a solution containing chloride or bromide counteranions (by anion exchange immediately before use), and the exclusive use of conductivity water gave reaction rates that were the same for a number of independent preparations of the complex. Even with extensive precautions and purification steps, rates were generally reproducible to within a standard deviation of only  $\sim 10\%$ , whereas our experience has been that similar procedures and analyses generally yield data with 3–5% standard deviations under similar conditions.

The reactants are both cations of the same charge type, and several series of experiments were performed to learn the type of medium best suited for minimizing salt effects. In particular the question was raised of whether the low precision of the rate constants could have been attributed to an unaccounted for change in medium, for instance in a series with varying

cobalt(III) concentration. Control of ionic strength may not be the most suitable parameter in reactions of two cations of high charge.<sup>13</sup> Moreover, specific cation effects have been noted in reactions between anions.<sup>14–16</sup>

A series of rate experiments was carried out at  $[\text{Co(III)}] = 0.003 M$  with  $0.020 M \text{H}^+$  at  $\mu = 0.053 M$  (maintained with  $\text{Li}^+$  or  $\text{Na}^+$  salts) and  $34.7^\circ$ ; starting tantalum concentrations were small relative to  $[\text{Co(III)}]$ , typically  $2\text{--}4 \times 10^{-5} M$ . Any given experiment followed pseudo-first-order kinetics quite closely; the rate constant (eq 2) was calculated from

$$-d[(\text{Ta}_6\text{Cl}_{12})^{2+}]/dt = k_1[(\text{Ta}_6\text{Cl}_{12})^{2+}] \quad (2)$$

the slope of a plot of  $\log(D - D_\infty)$  vs. time ( $D =$  absorbance) or from a plot based on the Guggenheim procedure. The reproducibility of duplicate runs was usually within an average deviation of 5–8%.

Values ( $M^{-1} \text{sec}^{-1}$ ) of the second-order rate constant  $k_2$  ( $k_1/[\text{Co(III)}]$ ) are as follows: with  $[\text{Cl}^-] = 0.047 M$ ,  $k_2 = 2.60 M^{-1} \text{sec}^{-1}$ ;  $[\text{Br}^-] = 0.047 M$ ,  $k_2 = 2.87$ ;  $[\text{ClO}_4^-] = 0.041 M + [\text{Cl}^-] = 0.006 M$ ,  $k_2 = 2.62$ ;  $[\text{NO}_3^-] = 0.034 M + [\text{Br}^-] = 0.013 M$ ,  $k_2 = 2.65$ ; and  $[\text{PF}_6^-] = 0.040 M + [\text{ClO}_4^-] = 0.004 M + [\text{Cl}^-] = 0.004 M$ ,  $k_2 = 2.42$ . The results of this and similar series of experiments with  $[\text{X}^-]$  and  $\mu$  simultaneously held constant served to establish that there was no *specific* anion effect within experimental error, in contrast to results cited above on reactions between anions.<sup>14–16</sup>

Over the range of cobalt(III)  $0.5\text{--}4 \times 10^{-3} M$ , values of  $k_2$  at  $\mu = 0.53 M$  and  $34.7^\circ$  were nearly constant. Such experiments covered a small range of anion concentrations of  $0.045\text{--}0.049 M$  and did not check the dependence of rate upon  $\mu$  and/or  $[\text{X}^-]$ . The average  $k_2$  was  $2.48 \pm 0.29 M^{-1} \text{sec}^{-1}$  in 55 runs.

A series of experiments was done in which a major portion of the MX electrolyte was replaced by a 1:2 electrolyte  $\text{BaBr}_2$ , up to  $0.012 M \text{Ba}^{2+}$ , at constant ionic strength. The average value of  $k_2$  was somewhat higher than before,  $2.99 M^{-1} \text{sec}^{-1}$  ( $\pm 0.41$  in ten experiments). Considering the precision obtainable in the rate constants, the difference of this value from that in MX solutions was not established. A further series of experiments was done with  $0.004\text{--}0.006 M \text{LaCl}_3$  used to replace all of the 1:1 electrolyte except a small concentration of HCl. At  $\mu = 0.051 M$  and  $34.7^\circ$ ,  $k_2$  was found to be  $2.40 \pm 0.03 M^{-1} \text{sec}^{-1}$  (six runs). The total concentration range of  $[\text{Cl}^-]$  in this series was  $0.030\text{--}0.036 M$ . The various experiments cited here served to establish that at constant ionic strength ( $\mu = 0.052 M$ ) the value of  $k_2$  was reasonably independent of anion concentration, which was varied from  $0.03$  to  $0.05 M$ , insensitive to the particular anions present and independent of the charge type of inert electrolyte used to maintain ionic strength.

(13) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

(14) R. J. Campion, P. King, and A. C. Wahl, 142nd National Meeting of the American Chemical Society, Division of Inorganic Chemistry, Atlantic City, N. J., Sept 1962, Paper 74.

(15) J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1920 (1957).

(16) E. V. Luoma and C. H. Brubaker, Jr., *Inorg. Chem.*, **5**, 1637 (1966).

The total variation in  $[H^+]$  was 0.0001–0.03  $M$ , with most runs at 0.01–0.02  $M$ . Within experimental error  $k_2$  was independent of  $[H^+]$  in this range. The concentration of  $H^+$  in any run was always sufficiently great,  $\geq 4[(Ta_6Cl_{12})^{2+}]_0$ , that the solutions remained acidic.

The proposed rate equation, eq 3, can be checked  $-d[(Ta_6Cl_{12})^{2+}]/dt = k_2[Co(NH_3)_4(OH_2)Cl^{2+}][(Ta_6Cl_{12})^{2+}]$  (3) further by studying the ionic medium effect upon  $k_2$ . The predicted slope of a plot  $\log k_2$  vs.  $\sqrt{\mu}$  is 4.07 according to the Brønsted-Debye-Hückel relation.<sup>17</sup> A series of experiments was carried out with the ionic strength contribution from various mixtures of HBr and BaBr<sub>2</sub> over the range  $0.009 \leq \mu \leq 0.052 M$ . A plot of  $k_2$  vs.  $\mu^{1/2}$  is shown in Figure 1. In the following relation (eq 4) between  $k_2$  and  $\mu$ , the value of

$$\log k_2 = \log k_2^0 + 0.51\Delta(Z^{\circ})^2/\mu^{1/2} \quad (4)$$

$k_2^0$  was  $1.35 M^{-1} \text{sec}^{-1}$  and the slope was 4.0, in agreement with the prediction of 4.07 from eq 3. This result confirmed the rate equation proposed before, eq 3, and in particular it ruled out a specific anion pathway,  $(Ta_6Cl_{12})^{2+} + Co(NH_3)_4(OH_2)Cl^{2+} + X^- \rightarrow (X^+)^{\ddagger}$ , for which the predicted slope is zero.

The temperature dependence of  $k_2$  was examined in a HCl-LaCl<sub>3</sub> medium of 0.05  $M$  ionic strength.  $k_2$  values ( $M^{-1} \text{sec}^{-1}$ ) were as follows: 25.0°,  $0.953 \pm 0.017$ ; 34.7°,  $2.40 \pm 0.03$ ; and 44.2°,  $4.07 \pm 0.35$ . According to the Eyring equation, values of  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  are  $13.5 \pm 0.6 \text{ kcal mole}^{-1}$  and  $-13 \pm 2 \text{ cal mole}^{-1} \text{ deg}^{-1}$ , respectively.

Several radiotracer experiments on reaction 1 were carried out employing chlorine-36. It was first established that anionic chloride ion does not exchange measurably with either  $(Ta_6Cl_{12})^{2+}$  or  $(Ta_6Cl_{12})^{3+}$  in a period of 13 hr at  $[Cl^-] = 0.050 M$  and  $[(Ta_6Cl_{12})] = 5 \times 10^{-4} M$ . A reaction of  $Co(NH_3)_4(OH_2)^*Cl^{2+}$  with  $Ta_6Cl_{12}^{2+}$ , each at a starting concentration of  $5 \times 10^{-4} M$ , was allowed to proceed for 13 hr, the time calculated for 96% reaction. At the end of this time  $Cl^-$  was separated from  $(Ta_6Cl_{12})^{3+}$  by cation exchange, and the latter was counted on the resin phase. The chloride solution was taken up by a column of anion-exchange resin (Dowex 1,  $Cl^-$  form) and also counted on the resin. The  $(Ta_6Cl_{12})^{3+}$  fraction had negligible activity above background, and the  $Cl^-$  fraction had the total activity of  $^*Cl$  added in  $Co(NH_3)_4(OH_2)Cl^{2+}$  within the precision of this method ( $\pm 20\%$ ). This experiment established that the oxidation-reduction in reaction 1 is not accompanied by chloride transfer from the Co(III) complex to the framework of the tantalum cluster ion.

Less detailed experiments were carried out for the oxidation of  $(Ta_6Cl_{12})^{2+}$  by several other cobalt(III) complexes. The stoichiometry of the oxidations in all of these cases appeared to be analogous to eq 1; no further oxidation to  $(Ta_6Cl_{12})^{4+}$  was detected. At

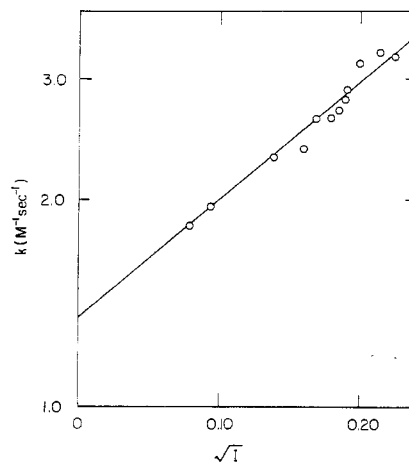
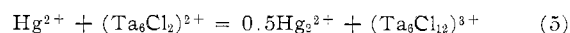


Figure 1.—The dependence of the second-order rate constant for the reaction of  $Co(NH_3)_4(OH_2)Cl^{2+}$  and  $(Ta_6Cl_{12})^{2+}$  upon ionic strength. The plot gives  $k_2$  (log scale) vs.  $\mu^{1/2}$ , according to eq 4.

34.7°, the rate constants ( $M^{-1} \text{sec}^{-1}$ ) were:  $Co(NH_3)_5-NCS^{2+}$ ,  $0.27 \pm 0.07$  ( $\mu = 0.05$ ); *cis*- $Co(NH_3)_4(OH_2)_2^{3+}$ ,  $1.11 \pm 0.05$  ( $\mu = 0.05$ );  $Co(NH_3)_5OH_2^{3+}$ ,  $0.14$  ( $\mu = 1.0$ ); *cis*- $Co(en)_2Cl_2^+$ ,  $3.5 \pm 0.2$  ( $\mu = 1.0$ ); *trans*- $Co(en)_2Cl_2^+$ ,  $4.0 \pm 0.1$  ( $\mu = 1.0$ );  $Co(NH_3)_5Cl^{2+}$ ,  $\sim 0.2$  ( $\mu = 0.05$ );<sup>18</sup>  $Co(NH_3)_5N_3^{2+}$ ,  $\sim 2.4$  ( $\mu = 0.05$ ). The rate experiments were not especially detailed, but they served to establish the rough pattern of reactivity.

**Mercury(II).**—The oxidation of  $(Ta_6Cl_{12})^{2+}$  by  $Hg^{2+}$  proceeded only to  $(Ta_6Cl_{12})^{3+}$ , eq 5. Studies were car-

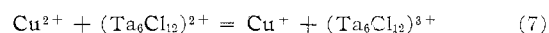


ried out at 25.0° in 1.00  $F$  perchloric acid ( $\mu = 1.0 M$ ). The initial concentration of  $(Ta_6Cl_{12})^{2+}$  was  $1.7 \times 10^{-4} M$  in all of the runs, and  $[Hg^{2+}]$  was varied from  $4 \times 10^{-4}$  to  $2 \times 10^{-3} M$ . The reaction followed pseudo-first-order kinetics to  $\geq 80\%$  completion, and the average  $k_{Hg}$  (eq 6) was  $3.46 \pm 0.25 M^{-1} \text{sec}^{-1}$  in



four experiments. In single experiments carried out at  $[H^+] = 0.50$  and  $0.25 M$ , using  $Ba(ClO_4)_2$  to maintain unit ionic strength, the values of  $k$  were  $2.68$  and  $2.07 M^{-1} \text{sec}^{-1}$ . The data are not sufficient to define the kinetics completely, but they do point to a decrease in rate with decreasing  $[H^+]$ .

**Copper(II).**—Oxidation of  $(Ta_6Cl_{12})^{2+}$  produced only a single oxidation step, even at high  $[Cu^{2+}]$  (eq 7). The



reaction was written giving  $Cu^+$  as the product. At the high copper(II) concentrations, 0.01–0.08  $M$ ,  $Cu(I)$  was stable with respect to disproportionation below  $\sim 10^{-4}$

(18) In the case of  $Co(NH_3)_5Cl^{2+}$  a great deal of difficulty was encountered in getting reproducible results. The scatter was high within any given set of experiments, and independent preparations of  $Co(NH_3)_5Cl^{2+}$  gave substantially different results, up to  $k_2 \sim 0.6 M^{-1} \text{sec}^{-1}$ . The value cited,  $k_2 = 0.2 M^{-1} \text{sec}^{-1}$ , was obtained in several preparations and was also the lowest value observed. Attempts were made to learn what substance was responsible for the effect of adding likely contaminants to either of the stock solutions. None of the substances chosen ( $Fe^{3+}$ ,  $Al^{3+}$ ,  $Co^{2+}$ ,  $Co(NH_3)_5OH_2^{3+}$ ,  $Co(NH_3)_5N_3^{2+}$ ) had a noticeable effect.

$M^{19,20}$  The kinetic studies were carried out at  $25.0^\circ$  in  $1.00 F$   $HClO_4$ . The reaction followed pseudo-first-order kinetics, and the computed second-order rate constant (eq 8) was  $k_{Cu} = 0.027 \pm 0.005 M^{-1} \text{ sec}^{-1}$ .

$$-d[(Ta_6Cl_{12})^{2+}]/dt = k_{Cu}[(Ta_6Cl_{12})^{2+}][Cu^{2+}] \quad (8)$$

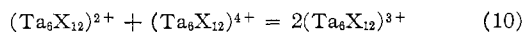
**Cerium(IV).**—Oxidation by Ce(IV) in perchloric acid readily proceeded in two stages: first to  $(Ta_6Cl_{12})^{3+}$ , then to  $(Ta_6Cl_{12})^{4+}$ . The stoichiometry was not investigated in detail beyond the limit  $[Ce^{IV}]_0/[(Ta_6Cl_{12})^{2+}]_0 = 2.0$ , but it appeared that subsequent oxidation reactions took place at higher Ce(IV) concentrations. The first stage of oxidation was extremely rapid. A single set of concentration conditions was studied:  $[(Ta_6Cl_{12})^{2+}]_0 = 6.6 \times 10^{-5} M$ ,  $[Ce(IV)]_0 = 9.7 \times 10^{-5} M$  in  $1.00 F$   $HClO_4$  at  $25.0^\circ$ . The experiment was repeated four times; assuming the reaction followed mixed-second-order kinetics (eq 9), we computed  $k_{Ce} = 1.5 \pm 0.3 \times 10^7 M^{-1} \text{ sec}^{-1}$ .

$$-d[(Ta_6Cl_{12})^{2+}]/dt = k_{Ce}[Ce(IV)][(Ta_6Cl_{12})^{2+}] \quad (9)$$

**Iodine, Iodate, and Bromate.**—Preliminary experiments indicated that oxidation to  $(Ta_6X_{12})^{3+}$  with  $I_2$  is a fairly rapid reaction. In  $1 F$   $HClO_4$  at  $25^\circ$  rough values of second-order rate constants are:  $(Ta_6Br_{12})^{2+}$ ,  $5 \times 10^2 M^{-1} \text{ sec}^{-1}$ ;  $(Ta_6Cl_{12})^{2+}$ ,  $7.4 \times 10^3 M^{-1} \text{ sec}^{-1}$ .

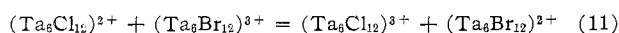
Each of the halate ion reactions is very definitely autocatalytic. We have not examined these reactions extensively, but it appeared that either the free elements or the oxyanions of lower oxidation number react at a higher rate than the halate itself.

**Reaction of  $(Ta_6X_{12})^{2+}$  and  $(Ta_6X_{12})^{4+}$ .**—Stopped-flow rate experiments were carried out on the re-proportionation reaction, eq 10, which is known<sup>2</sup> to lie well



toward the product side for both the bromide and the chloride cluster ions. In no experiment did we obtain a result indicating other than a completed reaction at the time of first observation. One experiment on the bromide compound had equal initial concentrations, each  $3.4 \times 10^{-5} M$  in  $1.0 F$  perchloric acid. If we set the rather conservative estimate of  $\leq 90\%$  completion within 5 msec, the computed second-order rate constant is  $\geq 5 \times 10^7 M^{-1} \text{ sec}^{-1}$ .

**Reaction of  $(Ta_6X_{12})^{2+}$  and  $(Ta_6X_{12})^{3+}$ .**—The position of equilibrium was examined in the reaction of bromide and chloride cluster ions of ionic charge  $3+$  and  $2+$  (eq 11). These experiments consisted of comparing



the observed spectra in the uv, visible, and ir regions with the individual components. Such spectral measurements were made on solutions prepared from roughly equimolar concentrations of  $(Ta_6Cl_{12})^{2+}$  and

$(Ta_6Br_{12})^{3+}$  and also from mixtures of the products. The spectrum of a mixture of  $(Ta_6Cl_{12})^{3+}$  and  $(Ta_6Br_{12})^{2+}$  was merely the sum of the independent spectrum of each component. The other mixture had an identical spectrum, but it was not the sum of the components from which it was made. We conclude that the equilibrium quotient for reaction 11 is greater than unity. Since small spectral discrepancies could not be evaluated precisely, we made conservative estimates from these data and placed a lower limit of  $K \geq 5$ . Thus  $(Ta_6Cl_{12})^{2+}$  is a more powerful reducing agent than its bromide analog by a potential of  $\geq 0.03 V$ .

Stopped-flow measurements were carried out at a wavelength at which a large absorbance change accompanied the reaction. One experiment had  $[(Ta_6Cl_{12})^{2+}]_0 = [(Ta_6Br_{12})^{3+}]_0 = 3.2 \times 10^{-5} M$  in  $1.00 F$  perchloric acid at  $25^\circ$ . No indication of a measurable rate was obtained; making the conservative estimate that  $\geq 95\%$  reaction occurred within 5 msec, we computed a second-order rate constant  $\geq 10^8 M^{-1} \text{ sec}^{-1}$ .

## Discussion

The original purpose of the investigation of the cobalt(III) complexes lay in comparing these cluster ion reactions with those of first-row reducing agents such as  $Cr^{2+}$ ,  $V^{2+}$ , and  $Fe^{2+}$ . We were not able to obtain data of an adequate degree of precision. The complex *cis*- $[Co(NH_3)_4(OH_2)Cl]^{2+}$  was studied most extensively; even in that reaction the reproducibility of kinetic data was less than anticipated. The tracer result established the lack of chloride transfer, and the participation of anions in the reaction was shown to be negligible.

Reactions of tantalum cluster ions may well prove extremely useful for studies of kinetic salt effects and medium effects. The high molar absorptivities permit precise rate measurements at exceptionally low concentrations. Moreover, one need not contend with acid-base equilibria, unlike aquometal ions. Hence, the lower limit of  $\mu$  is not fixed by some  $H^+$  concentration needed to suppress an acid dissociation equilibrium. The cobalt(III) complexes seemed to be ideally constituted for such studies, since acid dissociation equilibria likewise were not involved. Our inability to obtain rate data of high precision for these reactions limited the studies we had originally planned.

The unusual  $H^+$  dependence noted in the reactions of  $Hg^{2+}$  and  $Ta_6Br_{12}^{2+}$ , an increasing rate with increasing  $[H^+]$ , deserves further investigation.

The equilibrium quotient for the re-proportionation reaction is quite large. From crudely estimated potential values, we compute  $K$  for reaction 10 is  $10^{10}$ – $10^{15}$ . In contrast, the reaction of  $(Ta_6Cl_{12})^{2+}$  and  $(Ta_6Br_{12})^{3+}$  involves but a small free energy change. These two processes involve electron transfer between two cluster ions and are accompanied by a minimum of structural change. On the other hand, reactions with dissimilar oxidizing agents likewise involve little structural change for the cluster ion, and their low rates in comparison with cluster-cluster reactions are

(19) It has recently been shown, however, that even in the absence of a large excess of  $Cu^{2+}$ , disproportionation occurs slowly enough that metastable solutions can be prepared.<sup>20</sup>

(20) J. H. Espenson, K. Shaw, and O. J. Parker, *J. Am. Chem. Soc.*, **89**, 5730 (1967).

remarkable. The tentative conclusion we draw from these comparisons is that electron transfer between cluster ions has available a favorable mechanism that cannot operate for the nonsymmetrical reactions. In this connection it has been shown<sup>21</sup> that the formation

(21) O. Glemser and W. Höltje, *Angew. Chem. Intern. Ed. Engl.*, **5**, 736 (1966).

of polymolybdate anions from monomer units is also a very rapid process.

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## Coordination Compounds of Thallium(III). III. The Vibrational Spectra of Several Anionic and Neutral Complexes of Thallium(III) Chloride and Iodide and the Nature of These Species in the Solid State and in Polar Solvents

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Several new anionic and neutral complexes of thallium(III) chloride and iodide have been prepared. These include  $(C_2H_5)_4NTlCl_3I$ ,  $(C_2H_5)_4NTlCl_3B$ ,  $TlCl_3 \cdot 1.5pyz$ ,  $(TlX_3)_2 \cdot terpy$ ,  $TlCl_3 \cdot terpy$ , and  $TlI_3 \cdot py$ , where  $X = Cl$  or  $I$ ,  $B = 2,2'$ -bipyridyl or 1,10-phenanthroline,  $pyz = pyrazine$ ,  $terpy = 2,2',2''$ -terpyridyl, and  $py = pyridine$ . Molecular weight measurements in acetone and acetonitrile show that these and other complexes of thallium(III) [ $TlCl_3 \cdot 2py$ ,  $TlCl_3 \cdot 3\gamma$ -pic, and  $TlCl_3 \cdot 2DMSO$ ] are appreciably dissociated in polar media.  $TlCl_3 \cdot 3\gamma$ -pic,  $TlCl_3 \cdot 2py$ ,  $TlCl_3 \cdot 2DMSO$ , and  $TlX_3 \cdot bipy$  behave as weak electrolytes in these two solvents, whereas  $(TlX_3)_2 \cdot terpy$  are typical 1:1 electrolytes. The above solution data together with the far-infrared and Raman (for  $TlCl_3I^-$  and  $TlCl_3 \cdot 2DMSO$ ) spectra of the solid complexes indicate the structures:  $TlCl_3X^-$  ( $X = Br$  or  $I$ ), pseudo-tetrahedral;  $TlX_4B^-$  ( $X = Cl$  or  $Br$ ,  $B = bipy$  or  $phen$ ), *cis*- $MX_4L_2$  type structure;  $TlCl_3 \cdot 3\gamma$ -pic, *cis*- $TlCl_3N_3$ ;  $TlCl_3 \cdot 1.5pyz$ , *trans*- $TlCl_3N_3$ ;  $(TlX_3)_2 \cdot terpy$ ,  $[TlX_2 \cdot terpy]^+[TlX_4]^-$ ;  $TlCl_3 \cdot 2DMSO$ , *trans*-trigonal bipyramid;  $TlCl_3 \cdot 2py$ ,  $TlCl_3 \cdot bipy$ , and  $TlCl_3 \cdot phen$ , halogen-bridged dimers or polymers. Comparisons are made where possible with the analogous indium(III) halide systems.

### Introduction

In contrast to the considerable amount of data which has recently been accumulated on the acceptor properties of the indium(III) halides<sup>1-4</sup> and other salts, *e.g.*, nitrates and perchlorates,<sup>5,6</sup> relatively little work has been carried out on the analogous thallium(III) halide systems. Infrared and Raman spectral studies<sup>4,7-9</sup> have been used as a guide to the structure of adducts of indium(III) chloride, bromide, and iodide and complex halides of the type  $[InX_{4+n}]^{(1+n)-}$ , where  $n = 0, 1$ , or  $2$ . The development of a convenient method for the *in situ* preparation of thallium(III) chloride<sup>10</sup> has resulted in renewed interest in the chemistry and stereochemistry of thallium(III) halide systems. Following the work of Spiro<sup>11-13</sup> and Johnson

and Walton<sup>1</sup> on the Raman and infrared spectra of  $[TlX_{4+n}]^{(1+n)-}$ , it is now possible to establish the presence or absence of these particular species in other systems. In the absence of a single-crystal structure determination on any adduct of the indium(III) or thallium(III) halides, these spectroscopic techniques would seem to offer at present the most rewarding means of studying the nature of these species.

To investigate further the reactivity of the thallium(III) halides and the structure and stability of the resulting complexes, detailed molecular weight, conductivity, and far-infrared spectral studies ( $500$ – $33$   $cm^{-1}$ ) have been carried out. During this work several new complexes of thallium(III) chloride and iodide were isolated.

### Experimental Section

All reagents and solvents, with the exception of pyridine-2-carboxaldehyde 2-pyridylhydrazone (abbreviated PAPHY), were commercially available. The above named compound was prepared as described by Geldard and Lions.<sup>14</sup>

**Preparation of Compounds.**—The same method as that described previously<sup>1,10</sup> was used to prepare complexes of thallium(III) chloride; *i.e.*, thallos chloride, suspended in acetonitrile, was oxidized with chlorine and the appropriate reagent was then added to this solution.  $(C_2H_5)_4AsTlCl_4$ ,  $(C_2H_5)_4NTlX_4$  ( $X = Cl$  or  $Br$ ),  $TlCl_3 \cdot 2py$ ,  $TlCl_3 \cdot 2DMSO$ ,  $TlCl_3 \cdot bipy$ , and  $TlCl_3 \cdot phen$  were prepared as before.<sup>1,10</sup>

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