

TABLE I
 ELEMENTAL ANALYSES AND MOLECULAR WEIGHTS OF THE COMPOUNDS

Compound	% calcd			% found ^a			Mol wt	
	C	H	S	C	H	S	Calcd	Found ^b
Co(sacsac) ₂ P(C ₆ H ₅) ₃	57.62	5.00	21.98	57.81	5.02	21.88	583	597
Co(sacsac) ₂ As(C ₆ H ₅) ₃	53.59	4.66	20.44	53.67	4.76	20.16	620	618
Co(sacsac) ₂ Sb(C ₆ H ₅) ₃	49.90	4.34	19.06	49.86	4.40	18.87	675	655
Co(sacsac) ₂ Bi(C ₆ H ₅) ₃	44.15	3.83	16.84	44.35	3.81	17.00	762	696

^a Analyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn. ^b Cryoscopic in benzene.

 TABLE II
 SOLUTION OPTICAL SPECTRA AND MAGNETIC MOMENTS OF Co(sacsac)₂L

P(C ₆ H ₅) ₃	As(C ₆ H ₅) ₃		Sb(C ₆ H ₅) ₃		Bi(C ₆ H ₅) ₃		Co(sacsac) ₂		
	ν^a	ϵ^b	ν	ϵ	ν	ϵ	ν	ϵ	
{ 6,800	17	6,750	18.3	{ 6,800	25	{ 6,900	21	5,240	<10
{ 8,300 sh				{ 8,000 sh		{ 8,200 sh		6,750	22
11,000	23.5	11,000	25	11,100	27	11,100	29.5	10,000	31
{ 15,200 sh	525	{ 14,900 sh	270	{ 15,200 sh	526	{ 15,200 sh	490	{ 14,900 sh	350
17,700	4,330	17,800	2,360	17,900	4,120	17,800	4,620	17,500	4,070
21,800	3,790	21,850	3,680	21,900	3,540	21,900	3,980	21,650	3,240
{ 23,900 sh	4,100	{ 23,900 sh	4,380	{ 23,900 sh	3,650	{ 23,800 sh	4,130	{ 24,000 sh	5,000
28,500	14,500	27,800	13,300	27,800	12,900	27,500	13,700	28,000 sh	14,500
								29,500	15,000

μ_{eff} , BM

2.60

2.30

2.23

2.01

^a In cm⁻¹. Bands in the near-ir and visible regions. ^b In l. mol⁻¹ cm⁻¹.

 TABLE III
 SOLID-STATE OPTICAL SPECTRA (CM⁻¹) OF Co(sacsac)₂L AND [Co(AP)₂X]ClO₄

[Co(AP) ₂ Cl]-ClO ₄	[Co(AP) ₂ Br]-ClO ₄	[Co(AP) ₂ I]-ClO ₄	Co(sacsac) ₂ -P(C ₆ H ₅) ₃	Co(sacsac) ₂ -As(C ₆ H ₅) ₃	Co(sacsac) ₂ -Sb(C ₆ H ₅) ₃	Co(sacsac) ₂ -Bi(C ₆ H ₅) ₃
6,900	6,800	6,750	{ 6,800	{ 6,800	{ 6,800	{ 6,850
			{ 8,300 sh	{ 8,300 sh	{ 8,300 sh	{ 8,350 sh
11,000	11,000	11,000	11,000	11,100	11,100	11,100
12,500	{ 12,400 sh	{ 12,000 sh	{ 15,200 sh	{ 15,000 sh	{ 15,000 sh	{ 14,500
	{ 14,000	{ 15,700	{ 17,300	{ 17,500	{ 17,500	{ 17,450
21,900	21,600	20,750	21,650	21,900	21,900	21,850
		22,820	23,800 sh	23,900 sh	23,600	23,600
28,500	28,200	28,600	28,500 sh			

Co(sacsac)₂P(C₆H₅)₃, only a very slow quaternization takes place, and this is evident only after several minutes of standing at room temperature. The above data clearly show that the group V ligand is coordinated to cobalt.

The evidence at hand favors the square-pyramidal structure rather than the trigonal-bipyramidal arrangement, mostly on the basis of electronic spectra. The optical spectra of Co(sacsac)₂L, although shifted somewhat, are very similar to those of Co(AP)₂X⁺, both in solution and in the solid state. Arguments advanced by Dyer and Meek¹² for the interpretation of the optical spectra of Co(AP)₂X⁺ in terms of a square-pyramidal arrangement also apply here for Co(sacsac)₂L. On the other hand, electronic spectra of some known trigonal-bipyramidal molecules show spectra which are similar to each other (compare, e.g., Co(QP)X⁺⁷ with Co(CR)X⁺¹⁴) but are significantly different from the spectra of Co(sacsac)₂L and Co(AP)₂X⁺.

The similarity in electronic spectra taken in solution and in the solid state indicates that Co(sacsac)₂L, as well as Co(AP)₂X⁺, does not alter its structure upon dissolution. This also means that these compounds might possess only limited catalytic activity.

Acknowledgment.—We are grateful to Professor D. W. Meek of The Ohio State University for kindly supplying us with samples of [Co(AP)₂X]ClO₄.

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Electrochemistry of Tantalum Bromide Cluster Compound

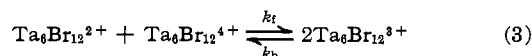
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Received July 9, 1970

The divalent tantalum bromide cluster ion Ta₆Br₁₂²⁺ has been shown to be chemically oxidizable to the tri- and quadrivalent ions Ta₆Br₁₂³⁺ and Ta₆Br₁₂⁴⁺ in aqueous solutions.^{2,3} Estimated values of the redox potentials for these two reactions



suggested a relatively large calculated value of K_{eq} for the reproporation reaction



(1) (a) Case Western Reserve University; (b) Iowa State University.

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

(3) (a) J. H. Espenson, *Inorg. Chem.*, **7**, 631 (1968); (b) J. H. Espenson and D. J. Boone, *ibid.*, **7**, 636 (1968).

The structurally similar $Ta_6Cl_{12}^{2+}$ cluster ion apparently exhibited redox behavior similar to that of the bromide cluster ion. Stopped-flow mixing experiments between the chloride and bromide ions indicated that the divalent chloride cluster was a stronger reducing agent than the bromide by *ca.* 0.03 V. All three oxidation states (2+, 3+, and 4+ ions) for both of these cluster ions appeared quite stable in well-degassed solutions. Based on crystallographic studies,⁴⁻⁶ no important structural or size differences exist among the different cluster ions. One might expect a higher solvated radius for the 4+ ion, but few other differences are likely. Consequently, the homogeneous and heterogeneous rate of electron transfer should be quite high, as so little activation energy is needed for structural reorganization.

It was therefore of interest to evaluate the electrochemical behavior of these cluster ions. In particular, the redox potentials for the two half-reactions (reactions 1 and 2), the reversibility of the electron-transfer reactions, and values of the K_{eq} for the reproporation reaction (eq 3) and for cross reactions between various species were calculated from data obtained by cyclic voltammetry, chronoamperometry, and spectroelectrochemistry.

Experimental Section

Aqueous 0.003 *F* stock solutions of the tantalum cluster cations $Ta_6Br_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ were prepared from purified samples of Ta_6Br_{14} , $Ta_6Cl_{14} \cdot 8H_2O$, or $K_4Ta_6Cl_{13}$ ⁷ and diluted as needed for each experiment. Because slow air oxidation occurs during storage, the diluted solutions containing 0.1 *M* perchloric acid were degassed by nitrogen (passed over hot copper turnings) and then electrolytically prerduced at an applied potential of 0.0 V *vs.* sce prior to each run. Reagent grade perchloric acid was used without further pretreatment. Doubly distilled water was used throughout.

The electrochemical cell was a conventional H cell utilizing a Pt foil working electrode, saturated calomel electrode (sce), and an auxiliary shielded electrode. The potentiostat and wave generator have been previously described.⁸ The current-time (*i-t*) function for chronoamperometry was monitored by a Midwestern Model 800-R light beam oscillographic recorder with a time resolution of 1 msec. A Cary Model 15 spectrophotometer was used for obtaining spectral data. Set-wavelength spectroelectrochemical experiments were performed with apparatus and cells already described.⁸ Both tin oxide and Pt optically transparent electrodes (ote) gave satisfactory results for the spectroelectrochemistry of $Ta_6Br_{12}^{2+}$.

Results and Discussions

A typical *i-E* curve for the oxidation of $Ta_6Br_{12}^{2+}$ in aqueous solution obtained using cyclic voltammetry at a stationary Pt electrode is shown in Figure 1. The general features are characteristic of two consecutive, one-electron transfer steps (EE mechanism), and both waves appear reversible. For both the first and second waves (E_{p1} and E_{p2}), the separations of the peak potentials of the forward and reverse waves were 58 mV in accord with that predicted for a reversible system.⁹ The formal electrode potential, E° , is related to the potential at 0.852 of the peak current (i_p) for a reversible *i-E* wave (stationary electrode, semiinfinite linear diffusion conditions). Values of $E_{0.852}$ for first and second

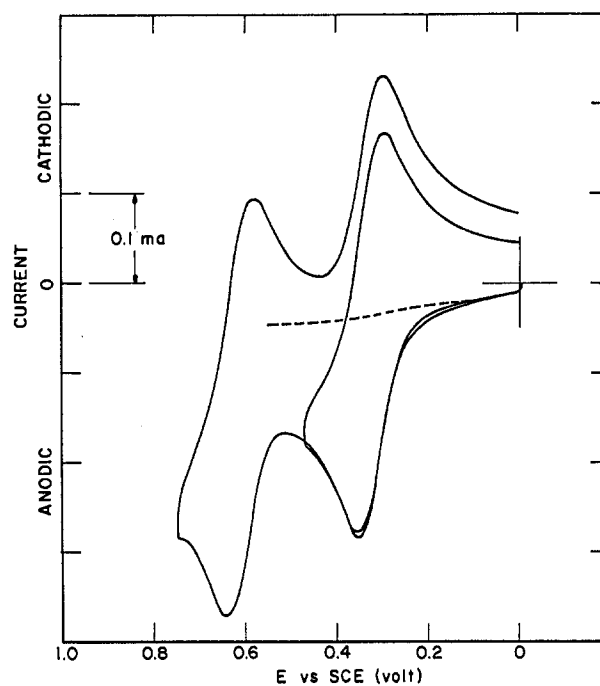


Figure 1.—The cyclic voltammetry *i-E* curves for the one-electron oxidation and the two consecutive one-electron step oxidation are shown for 7×10^{-4} *M* $Ta_6Br_{12}^{2+}$ in 0.1 *F* $HClO_4$ solution at a planar platinum electrode (area 2.5 cm²). The dotted curve is background *i-E* at the same scan rate (0.04 V/sec) in the absence of $Ta_6Br_{12}^{2+}$.

waves are $+0.35 \pm 0.01$ and $+0.65 \pm 0.01$ V *vs.* sce at 25°. The difference between these two potentials gives a calculated K_{eq} (reaction 3) of 1.08×10^5 . The plot of i_p *vs.* square root of scan rate for the oxidation of $Ta_6Br_{12}^{2+}$ to $Ta_6Br_{12}^{3+}$ obtained by linear-sweep voltammetry was linear (for a scan rate range of 0.04–0.64 V/sec) when the i_p values were corrected for background currents. These latter currents were obtained at the same scan rates in the absence of $Ta_6Br_{12}^{2+}$. When this plot was extrapolated to a zero scan rate, a zero intercept was obtained.

From chronoamperometry (potential stepped from 0.0 to +0.40 V *vs.* sce), the i *vs.* $t^{-1/2}$ plot was linear, and a diffusion coefficient, D , of 7.37×10^{-6} cm² sec⁻¹ at 25° was calculated. Using this value as a reference, the diffusion coefficients for the 3+ and 4+ species were calculated as 5.5×10^{-6} and 3.7×10^{-6} cm² sec⁻¹ at 25° from *i-E* curves obtained from cyclic voltammetry. The peak oxidative (3+ to 4+) and the reductive (4+ to 3+) currents were corrected for the background current by extrapolating the base of the *i-E* curves by the potential-hold method described by Adams.⁹ The last two values of diffusion coefficients are estimated to be accurate to $\pm 10\%$. The temperature dependence of the diffusion coefficient for the 2+ species evaluated by chronoamperometry gave a linear $\log D$ *vs.* $1/T$ plot. The activation energy for diffusion, 1.2 kcal, was surprisingly low.

In the visible region of the spectrum, it is difficult to perform spectroelectrochemical experiments using transmission spectroscopy at the ote because of the strong absorption by the parent $Ta_6Br_{12}^{2+}$ ion. It is convenient, however, to employ internal reflection spectroscopy¹⁰ (irs) where the light beam is reflected at the

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 (5) D. Bauer and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, **361**, 259 (1968).
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 (7) P. J. Kuhn and R. E. McCarley, *Inorg. Chem.*, **4**, 1482 (1965).
 (8) J. W. Strojek and T. Kuwana, *J. Electroanal. Chem.*, **16**, 471 (1968).
 (9) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969; see discussion, Chapter 5.

(10) N. Winograd and T. Kuwana, *J. Electroanal. Chem.*, **23**, 333 (1969).

electrode surface-solution interface. The beam enters the solution from the direction of the electrode and penetrates and samples the solution for only a short distance of ca. 1000 Å. Thus, the conversion rate of $\text{Ta}_6\text{Br}_{12}^{2+}$ to $\text{Ta}_6\text{Br}_{12}^{3+}$ was monitored during a chronoamperometric experiment when the potential was stepped about 100 mV more positive than $(E_p)_1$ at a Pt ote. The monitoring wavelength of 620 nm for the absorption of $\text{Ta}_6\text{Br}_{12}^{2+}$ was used and the value of the molar extinction coefficient, ϵ , was $6000 \text{ M}^{-1} \text{ cm}^{-1}$. The irs absorbance-time behavior conformed to that expected for a diffusion-controlled electrode reaction with no complications. A value of $\epsilon D^{1/2}$ of $1.2 \text{ M}^{-1} \text{ sec}^{-1}$ at 620 nm was calculated. Taking advantage of the fact that the potential can be stepped to a value where the 2+ ion can be oxidized to the 4+ species, Winograd¹¹ has evaluated the k_t for reaction 3 using irs monitoring of the 2+ species. He reported a value of $k_t = 6.9 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°. This compares favorably to the value $k_t \geq 5 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ reported earlier^{3b} for a 1 M HClO_4 solution.

From the temperature dependence of the difference between the formal electrode potentials ($E^{\circ'}$) of the two waves, the thermodynamic parameters for reaction 3 were evaluated. The calculated values of K_{eq} for reaction 3 are plotted as a logarithmic function of T^{-1} ($^{\circ}\text{K}^{-1}$) in Figure 2. Usual treatment of the data

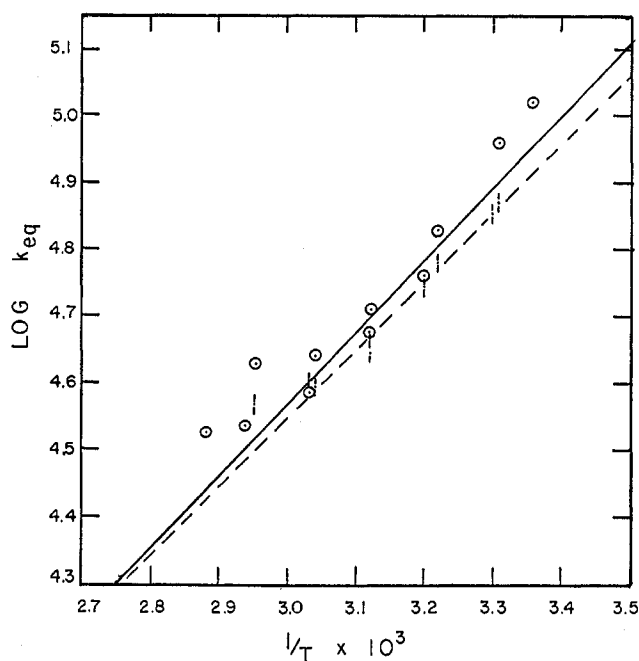


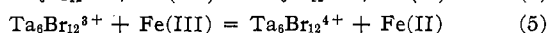
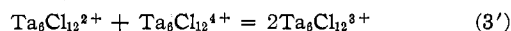
Figure 2.—Plots of $\log K_{eq}$ vs. $1/T$; the circled points represent K_{eq} calculated by taking $(E_{0.852})_2 - (E_{0.852})_1$ whereas the other points are K_{eq} calculated by taking $(E_p)_2 - (E_p)_1$. The solid line is drawn from the least squares of the circled points. All data for calculations in the text are taken using this line. For comparison purposes, the least-squares line is drawn (broken line) for the points determined from the E_p values.

(taken from the solid line in Figure 2) gives $\Delta H = 4.99 \pm 0.46 \text{ kcal/mol}$, $\Delta G = -6.76 \pm 0.86 \text{ kcal/mol}$, and $\Delta S = 39 \pm 4 \text{ eu}$ for this reaction. The value of K_{eq} for reaction 3 at 25° is equal to 9.02×10^4 as taken

from the least-squares line of the data points in the plot of Figure 2.

The fairly large positive entropy probably reflects structure-breaking changes in going from $\text{Ta}_6\text{Br}_{12}^{4+}$ to $\text{Ta}_6\text{Br}_{12}^{3+}$. This may involve the solvent as well as counterions around the more highly charged cation. This change is also reflected in the radii calculated from the diffusion coefficients using the Stokes-Einstein relationship ($D = kT/6\pi r$) where the values of radii are 3.3, 4.4, and 6.7 Å for the 2+, 3+, and 4+ ions, respectively. The crystal radius of the 2+ bromide cluster is 3.7 Å as calculated from X-ray data.^{12,13}

The $\text{Ta}_6\text{Cl}_{12}^{2+}$ cluster behaves similarly to the bromide with the exception that repeated cyclic scans are not as reproducible as with the bromide cluster. The $E_1^{\circ'}$ and $E_2^{\circ'}$ are 0.25 and 0.59 V vs. sce. These values of potential now allow the calculation of equilibrium quotients (K_{eq}) for the reproporationation reaction, eq 3', and other reactions, eq 4-6, involving cross electron transfers. The results are summarized in Table I.



The present data support previous chemical studies (see Table I) and confirm the earlier predictions that

TABLE I
SUMMARY OF FORMAL ELECTRODE POTENTIALS AND EQUILIBRIUM QUOTIENTS INVOLVING TANTALUM BROMIDE AND CHLORIDE CLUSTER IONS AT 25°

Reactions	Bromide cluster	Chloride cluster
I. Electrode Potentials, V (vs. Sce)		
1, 1'	0.35 ± 0.01	0.25
2, 2'	0.65 ± 0.01	0.59
II. Equilibrium Quotients ^a		
3, 3'	1.08×10^5	5.7×10^4
4, 4' ^b	2.7×10^2	1.3×10^4
5, 5' ^b	2.2×10^{-3}	0.023 (0.018)
6	49 ($5 < K < 20$)	

^a Previously reported estimates^{2,3} are in parentheses; reactions in 0.1 F HClO_4 . The primed reactions are for the analogous $\text{Ta}_6\text{Cl}_{12}$ reactions. ^b $E^{\circ'}$ is +0.735 V vs. nhe for $\text{Fe(III)} + e^- = \text{Fe(II)}$ in 0.1 F HClO_4 solution: G. F. Smith, *Anal. Chem.*, **23**, 925 (1951). Value for sce taken as +0.242 V vs. nhe.

the cluster ions remain intact during electron transfer and are in an equilibrium involving the 2+, 3+, and 4+ ions. For the $\text{Ta}_6\text{Br}_{12}^{2+}$ cluster ion, the electron transfer appears to be rapid; the $i-E$ curves for cyclic voltammetry were in accord with reversible behavior. The homogeneous electron-transfer rates are also fast as determined for the reproporationation equilibrium, eq 3. These results support the conclusion that there appears to be a minimal structure change occurring particularly between the 2+ and the 3+ ions.

Acknowledgment.—The authors gratefully acknowledge the support provided by NSF Grant No. GP. 9306. N. E. C. wishes to acknowledge support during the summer of 1969 by an NSF sponsored undergraduate research participation program.

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