Electrochemical and Spectroscopic Characterization of {Ta$_6$Cl$_{12}$}$^{z+}$ Chloride Clusters in Acetonitrile and in the Aluminum Chloride−1-Methyl-3-ethylimidazolium Chloride Molten Salt

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The electrochemistry and electronic absorption spectroscopy of the anionic chloride complexes derived from the metal−metal bonded {Ta$_6$Cl$_{12}$}$^{z+}$ ($z = 2-5$) clusters were examined in CH$_3$CN/[(n-Bu)$_4$N]PF$_6$ at 23 °C and in the room-temperature chloroaluminate molten salt, aluminum chloride−1-methyl-3-ethylimidazolium chloride (AlCl$_3$−[MeEtim]Cl) at 40 °C. The following electrochemical reactions were identified in the former solvent (potentials versus Ag/ 0.10 M Ag$^+$): [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ (red-orange) ⇌ [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{-}$ (unstable) +e$^-$, $E_{1/2}$ = 1.19 V; [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ + e$^-$ ⇌ [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-}$ (yellow), $E_{1/2}$ = −0.28 V; [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-}$ (yellow) + e$^-$ ⇌ [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ (green), $E_{1/2}$ = −0.84 V; [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ + CH$_3$CN ⇌ [(Ta$_6$Cl$_{12}$)Cl$_5$(CH$_3$CN)]$^{3-}$ (green) + Cl$^-$. The replacement of chloride ion by CH$_3$CN in the [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ complex in the last step shown above takes place in a slow homogeneous reaction that is coupled to the [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-/4-}$ electrode reaction. This homogeneous reaction is observed on the time scale of bulk controlled-potential electrolysis in CH$_3$CN/[(n-Bu)$_4$N]PF$_6$ without added chloride ion, but not during voltammetric experiments. The addition of a large excess of chloride ion to a solution containing [(Ta$_6$Cl$_{12}$)Cl$_5$(CH$_3$CN)]$^{3-}$ converts this complex back to [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$. In the acidic AlCl$_3$−[MeEtim]Cl melt, two reversible redox reactions, analogous to the {Ta$_6$Cl$_{12}$}$^{4+/3+}$ and {Ta$_6$Cl$_{12}$}$^{3+/2+}$ reactions seen in CH$_3$CN, were found at $E_{1/2}$ = 1.16 and 0.79 V (versus Al/Al(III) in the 66.7−33.3 mol % melt), respectively. However, intersolvent comparisons of the $E_{1/2}$ of these reactions referenced to the Fe(cp)$^{0/+}$ couple indicated that both are shifted positively by more than 1 V in the molten salt relative to CH$_3$CN/[(n-Bu)$_4$N]PF$_6$, suggesting replacement of labile chloride ions on the [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{(6-z)-}$ ($z = 2-4$) clusters with [AlCl$_4$]$^-$ during dissolution in acidic melt to produce species with the general formula, [(Ta$_6$Cl$_{12}$)Cl$_y$(AlCl$_4$)$_{6-y}$]$^{(6-z)-}$ ($y \leq 6$). The Stokes-Einstein products of the [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{(6-z)-}$ ($z = 3$ and 4) clusters in CH$_3$CN/[(n-Bu)$_4$N]PF$_6$ were nearly the same with an average value of ca. 10 × 10^{-11} g cm s^{-2} K^{-1}. This value is very close to that found for the corresponding anionic niobium clusters in a previous investigation conducted in basic AlCl$_3$−[MeEtim]Cl.

Introduction

The group 5 hexanuclear metal clusters possess a central octahedron of metal−metal bonded metal atoms bridged by π-donor ligands such as halide. There are sixteen electrons available for bonding in these clusters, and these electrons are distributed among eight skeletal electron pairs, producing three-center, two-electron bonds between metal atoms and bridging halides.[4] These halide bridges extend along each of the 12 edges of the octahedron, resulting in a robust M$_6$X$_{12}$ structural unit. A single coordination site directed away from the center of the octahedron is present on each of the metal atoms that constitute the core of the cluster. The anionic halide complexes of the core cluster, e.g., [(M$_6$X$_{12}$)X$_6$]$^{(6-z)-}$, are obtained when these coordination sites are occupied by terminal halide ions. The redox reactions associated with these clusters are conveniently described in terms of the oxidation level of the core, e.g., {M$_6$X$_{12}$}$^{z+}$, without consideration of these terminal ligands.

However, it is extremely unusual to find the core cluster devoid of ligands at these positions. In fact, the so-called "solvated cations" of these clusters found in aqueous solutions are probably coordinated to H$_2$O at these sites.

In a previous article,[5] we reported the electrochemical and spectroscopic characterization of clusters derived from the {Nb$_6$Cl$_{12}$}$^{z+}$ ($z = 1$ to 4) core in both basic and acidic AlCl$_3$-[MeEtim]Cl melt.[6] In basic melt, the overall electrochemical

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(4) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th ed.; Wiley: New York, 1988; p 1079.

(5) Quigley, R.; Barnard, P. A.; Hussey, C. L.; Seddon, K. R. *Inorg. Chem.,* **1992,** *31,* 1255.
(6) The physical and electrochemical properties of this nominally aprotic, ionic solvent have been reviewed at length; see: (a) Chum, H. L. ; Osteryoung, R. A. In *Ionic Liquids;* Inman, D., Lovering, D. G., Eds.; Plenum: New York, 1981; pp 407−423. (b) Hussey, C. L. In *Advances in Molten Salt Chemistry;* Mamantov, G., Mamantov, C. B., Eds.; Elsevier: Amsterdam, 1983; Vol. 5, pp 185−230. (c) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques;* Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. 1, pp 55−78. (d) Osteryoung, R. A. In *Molten Salt Chemistry, An Introduction and Selected Applications;* Mamantov, G., Marassi, R., Eds.; NATO ASI Series C; Reidel: Dordrecht, The Netherlands, 1987; Vol. 202, pp 329−364. (e) Hussey, C. L. In *Chemistry of Nonaqueous Solutions: Recent Advances;* Popov, A. I., Mamantov, G., Eds.; VCH: New York, 1994; pp 227−275. "Basic" melts result when AlCl$_3$ is combined with a molar excess of the organic salt; these melts contain chloride ion that is not covalently bound to aluminum. "Acidic" melts are produced by adding the organic salt to a molar excess of AlCl$_3$, and they are Lewis acidic owing to the presence of coordinatively unsaturated species such as Al$_2$Cl$_7^-$.
(7) Bachtler, M.; Rockenberger, J.; Freyland, W.; Rosenkilde, Chr.; Ostvold, T. *J. Phys. Chem.* **1994,** *98,* 742.

scheme for anionic complexes derived from this niobium cluster unit is

$$[(Nb_6Cl_{12})Cl_6]^{4-} \xrightleftharpoons[+e^-]{-e^-} [(Nb_6Cl_{12})Cl_6]^{3-} \xrightleftharpoons[+e^-]{-e^-} [(Nb_6Cl_{12})Cl_6]^{2-} \quad (1)$$

$$+e^- \downarrow \uparrow -e^-$$
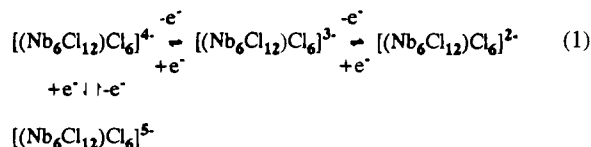
$$[(Nb_6Cl_{12})Cl_6]^{5-}$$

However, in acidic melt, only species containing the {Nb$_6$Cl$_{12}$}$^{z+}$ core with $z = 2$ to 4 were accessible within the electrochemical window of the solvent.

The absorption spectroscopy of Na$_4$[(Ta$_6$Cl$_{12}$)Cl$_6$] was investigated in the NaCl—CsCl eutectic at 570 °C by Bachtler *et al.*[7] However, changes in the spectra of this compound in this melt suggested slow decomposition of the [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ ion to other tantalum species at this temperature.

Although the electrochemistry of complexes derived from the {Nb$_6$Cl$_{12}$}$^{z+}$ core cluster is now firmly established, there is a paucity of such information for species derived from the related {Ta$_6$Cl$_{12}$}$^{z+}$ clusters, especially the chloride complexes. The first electrochemical investigation of hexameric tantalum clusters was reported by Cooke *et al.*,[8] who examined the voltammetry of the solvated cations, [(Ta$_6$X$_{12}$)(H$_2$O)$_p$]$^{z+}$ (X = Br and Cl), in aqueous 0.1 M HClO$_4$ at a platinum electrode. This study revealed that the [(Ta$_6$X$_{12}$)(H$_2$O)$_p$]$^{2+/3+}$ and [(Ta$_6$X$_{12}$)(H$_2$O)$_p$]$^{3+/4+}$ electrode reactions are reversible and that cations with $z = 2$, 3, and 4 are stable in degassed aqueous solutions. In the case of the chloride clusters, the voltammetric half-wave potentials, $E_{1/2}$, of these reactions are 0.25 and 0.59 V, respectively, versus the SCE. Klendworth and Walton[9] examined the electrochemistry of the tertiary phosphine complex, [(Ta$_6$Cl$_{12}$)Cl$_2$(P-n-Pr$_3$)$_4$] (n-Pr$_3$ = n-propyl), in dichloromethane and the oxidized form of this complex, [(Ta$_6$Cl$_{12}$)Cl$_2$(P-n-Pr$_3$)$_4$]$^{2+}$, in acetonitrile at a platinum bead electrode. Cyclic voltammograms of the former revealed quasireversible couples at $E_{1/2} = 0.77$ and 0.19 V versus SCE, corresponding to the [(Ta$_6$Cl$_{12}$)Cl$_2$(P-n-Pr$_3$)$_4$]$^{2+/+}$ and [(Ta$_6$Cl$_{12}$)Cl$_2$(P-n-Pr$_3$)$_4$]$^{+/0}$ electrode reactions, respectively. The [(Ta$_6$Cl$_{12}$)Cl$_2$(P-n-Pr$_3$)$_4$]$^{0/-}$ reaction can be observed in acetonitrile at $E_{1/2} = -1.60$ V, but the monoanion product is only stable on the time scale of cyclic voltammetry. In this article, we report the results of electrochemical and spectroscopic investigations of chloride complexes derived from the dodecakis-(μ-chloro)hexatantalum(z+) core, {Ta$_6$Cl$_{12}$}$^{z+}$, in both acetonitrile and acidic AlCl$_3$—[MeEtim]Cl.

Experimental Section

Apparatus. Cyclic and rotating disk electrode (RDE) voltammetry and controlled-potential electrolysis (CPE) were carried out with an EG&G Princeton Applied Research Corp. (PARC) Model 173 potentiostat/galvanostat, PARC Model 179 digital coulometer module, and PARC Model 175 universal programmer. RDE experiments were conducted with a Pine Model AFASR electrode rotator. Electrochemical data were displayed on either a Houston Instruments Model 100 or a Linseis Model 1600 X-Y/Y-t recorder. Electronic resistance compensation was employed during all voltammetric experiments.

Electrochemical experiments conducted in CH$_3$CN were performed at room temperature (23 ± 2 °C) in a small three-compartment Pyrex glass cell under a flowing stream of CH$_3$CN-saturated, oxygen-free, dry N$_2$. Voltammetric experiments with {Ta$_6$Cl$_{12}$}$^{z+}$ cluster compounds were conducted at a small platinum disk working electrode with a Kel-F body (geometrical surface area = 0.0214 cm^2), whereas those involving the oxidation of [MeEtim]Cl were carried out at a Pine Instruments platinum disk electrode (geometrical area = 0.196 cm^2); in each case the counter electrode was a concentric tungsten wire spiral. CPE experiments were carried out at a concentric coil of platinum wire.

The reference electrode used during these experiments was a silver wire immersed in a 0.10 M solution of AgNO$_3$ (Ag/ 0.10 M Ag$^+$); this electrode was separated from the bulk solution by means of a porous Vycor plug.

Electrochemical experiments involving the AlCl$_3$—[MeEtim]Cl melt were performed at 40.0 ± 0.2 °C in a nitrogen-filled glovebox system. This glovebox system and the method used to monitor the moisture and oxygen content of the box atmosphere were described previously.[5] The electrochemical cell, the furnace used to heat the cell, the Pyrex glass/glassy carbon disk working electrode (geometrical surface area = 0.0707 cm^2), and the reference and counter electrodes that were used in these experiments were identical to those described in a previous article.[10] CPE experiments were carried out in a glassy carbon cup, which served as the working electrode.

Electronic absorption spectra were recorded in either 1.00 or 2.00 mm path length fused silica cells fitted with air-tight Teflon caps by using a Perkin-Elmer Model 3840 Lambda Array spectrophotometer operated in the high-performance mode or with a Perkin-Elmer Hitachi Model 200 UV—vis spectrophotometer.

Chemicals. The methods used to prepare and/or purify AlCl$_3$ and [MeEtim]Cl were the same as those described in previous publications.[5,11] The 60.0—40.0 mol % AlCl$_3$—[MeEtim]Cl melt was purified by constant-current electrolysis between aluminum electrodes.[12] CH$_3$-CN was dried over 3A molecular sieves, distilled from CaH$_2$, passed through a column of activated alumina, and stored over fresh 3A sieves until needed. The supporting electrolyte for experiments involving CH$_3$-CN was tetra(n-butyl)ammonium hexafluorophosphate, [(n-Bu)$_4$N]PF$_6$. This salt was prepared and purified according to standard procedures.[13] The kinematic viscosity and density of the CH$_3$CN + 0.20 M [(n-Bu)$_x$N]-PF$_6$ solutions used in this study were determined at 23 ± 1 °C by using a No. 25 Cannon-Fenske viscometer (Cannon Instrument Co.) and a standard 10 mL pycnometer (Kimble, No. 15123—10), respectively. Both were calibrated with distilled water at the temperature of the measurement.

The hydrated cluster (Ta$_6$Cl$_{12}$)Cl$_2$·8H$_2$O was synthesized using the method suggested by Koknat *et al.*[14] This compound served as the starting material for the preparation of both the [MeEtim]$_3$[(Ta$_6$Cl$_{12}$)Cl$_6$] and the [MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$] salts. A detailed description of the procedures used to prepare these compounds is available.[15]

Results and Discussion

Acetonitrile. The [MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$] salt was found to be completely insoluble in basic AlCl$_3$—[MeEtim]Cl at 40 °C. Some slight solubility of this compound was noted when the temperature was raised to about 150 °C, but the concentration of cluster in the resulting solution was judged to be too small for meaningful electrochemical studies. However, this compound dissolved readily in acetonitrile to produce a red-orange solution. Data taken from the absorption spectra of such solutions are presented in Table 1 along with literature data for solutions known to contain the [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ ion. Comparison of these data confirms the presence of this ion in the CH$_3$-CN solution after the dissolution of the aforementioned salt.

Cyclic voltammograms of a solution of [MeEtim]$_2$[(Ta$_6$-Cl$_{12}$)Cl$_6$] in CH$_3$CN/[(n-Bu)$_4$N]PF$_6$ are shown in Figure 1. A scan initiated toward negative potentials reveals two reduction waves with peak potentials, E_p^c, of ca. −0.30 and −0.87 V, whereas a scan initiated toward positive potentials discloses a single oxidation wave with $E_p^a = 1.22$ V. Reverse currents are associated with the two reduction waves and the oxidation

(8) Cooke, N. E.; Kuwana, T.; Espenson, J. *Inorg. Chem.* **1971**, *10*, 1081.
(9) Klendworth, D. D.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 1151.

(10) Scheffler, T. B.; Hussey, C. L. *Inorg. Chem.* **1984**, *23*, 1926.
(11) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263.
(12) Xu, X.-H.; Hussey, C. L. *J. Electrochem. Soc.* **1993**, *140*, 618.
(13) Fry, A. J.; Britton, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T., Heineman, W. R., Eds.; Dekker: New York, 1984; p 378.
(14) Koknat, F. W.; McCarley, R. E. *Inorg. Chem.* **1974**, *13*, 295.
(15) Quigley, R. D.Phil. Thesis, University of Sussex, 1993
(16) Fleming, P. B.; McCarley, R. E. *Inorg. Chem.* **1970**, *9*, 1347.
(17) Khun, P. J.; McCarley, R. E. *Inorg. Chem.* **1965**, *4*, 1482.

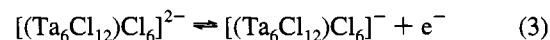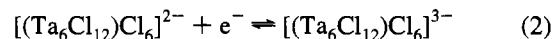**Table 1.** Electronic Absorption Spectroscopic Data for Hexameric Tantalum Clusters

solute/starting material	solvent	λ, nm (ϵ, M^{-1} cm^{-1})	ref
		{Ta$_6$Cl$_{12}$}$^{4+}$ Core	
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]	CH$_3$CN	246 (3.2 × 10^4), ~280,^{a} 366 (2.8 × 10^4), 441 (2.5 × 10^3), ~525,^{a} ~850 (1.5 × 10^3)	this work
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]	CH$_3$CN + 0.20 M [(n-Bu)$_4$N]PF$_6$ + 0.33 M [MeEtim]Cl	~280,^{a} 367 (3.0 × 10^4), 443 (2.6 × 10^3), ~525,^{a} ~850 (1.6 × 10^3)	this work
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]	60.0−40.0 AlCl$_3$−[MeEtim]Cl	~280,^{a} 343 (1.9 × 10^4), 405 (2.4 × 10^3), ~455,^{a} 690 (8.9 × 10^2)	this work
[(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$	(CH$_3$)$_2$O	248 (1.9 × 10^4), 285 (8.4 x 10^3), 369 (2.7 × 10^4), 444 (2.5 × 10^3), 521 (1.0 × 10^3), 844 (1.3 × 10^3), 990 (3.2 × 10^2), 1157 (5.0 × 10^1)	16
		{Ta$_6$Cl$_{12}$}$^{3+}$ Core	
[MeEtim]$_3$[(Ta$_6$Cl$_{12}$)Cl$_6$]	CH$_3$CN	242 (2.8 × 10^4), ~280,^{a} 356 (2.7 × 10^4), 430 (3.0 × 10^3), ~530,^{a} 763 (1.9 × 10^3), 873 (3.5 × 10^3)	this work
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]^b	CH$_3$CN + 0.20 M [(n-Bu)$_4$N]PF$_6$	240 (2.6 × 10^4), ~280,^{a} 356 (2.6 × 10^4), 431 (2.8 × 10^3), ~530,^{a} 763 (2.0 × 10^3), 872 (3.7 × 10^3)	this work
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]^b	CH$_3$CN + 0.20 M [(n-Bu)$_4$N]PF$_6$ + 0.33 M [MeEtim]Cl	~280,^{a} 355 (2.7 × 10^4), 428 (2.7 × 10^3), ~530,^{a} 762 (2.0 × 10^3), 872 (3.7 × 10^3)	this work
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]^c	60.0−40.0 AlCl$_3$−[MeEtim]Cl	261 (1.1 × 10^4), ~280,^{a} 332 (1.7 × 10^4), 394 (2.3 × 10^3), 718 (2.8 × 10^3), ~900 (2.0 × 10^3)	this work
[(Ta$_6$Cl$_{12}$)(H$_2$O)$_p$]$^{3+}$ ^{d}	C$_2$H$_5$OH	235 (1.6 × 10^4), 275 (8 x 10^3), 345 (1.45 × 10^4), 431 (2.2 × 10^3), 735 (1.7 × 10^3), 826 (2.0 × 10^3), 943 (1.5 × 10^3)	16
		{Ta$_6$Cl$_{12}$}$^{2+}$ Core	
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]^e	CH$_3$CN + 0.20 M [(n-Bu)$_4$N]PF$_6$ + 0.33 M [MeEtim]Cl	285 (9.1 × 10^3), 347 (2.7 × 10^4), 420 (3.7 × 10^3), ~490,^{a} 676 (5.0 × 10^3), 800 (2.9 × 10^3)	this work
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]^e	CH$_3$CN + 0.20 M [(n-Bu)$_4$N]PF$_6$	237,^{a} 287,^{a} 346, 416, ~490,^{a} 674, 796	this work
[MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$]^f	60.0−40.0 AlCl$_3$-[MeEtim]Cl	269 (1.1 × 10^4), 289,^{a} 326 (1.3 × 10^4), 385 (2.9 × 10^3), ~450,^{a} 664 (4.2 × 10^3), 783 (2.3 × 10^3)	this work
[(Ta$_6$Cl$_{12}$)(H$_2$O)$_p$]$^{2+}$ ^{d}	H$_2$O	329, 398, 470,^{a} 637, 755	17
[(Ta$_6$Cl$_{12}$)(H$_2$O)$_p$]$^{2+}$ ^{d}	(CH$_3$)$_2$SO	237 (2.0 × 10^4), 290 (8 × 10^3), 334 (3.0 × 10^4), 400 (6 × 10^3), 490 (1.2 × 10^3), 658 (3.8 × 10^3), 787 (2.2 × 10^3)	16

^{a} Shoulder. ^{b} After reduction at −0.50 V vs Ag/0.10 M Ag$^+$. ^{c} After reduction at 0.98 V vs Al/Al(III). ^{d} Solvated cation. ^{e} After reduction at −1.10 V vs Ag/0.10 M Ag$^+$. ^{f} After reduction at 0.50 V vs Al/Al(III).

wave. No other waves were observed within the potential window of the solvent/supporting electrolyte. Cyclic voltammetric examination of the first reduction wave and its associated oxidation wave over the range of scan rates extending from 0.020 to 0.200 V s^{-1} revealed that $E_p{}^c$ and the cathodic peak current function, $i_p{}^c/v^{1/2}$, where v is the scan rate, were independent of v. In addition, the anodic to cathodic peak current ratio, $i_p{}^a/i_p{}^c$, calculated by using Nicholson's empirical method,[18] was 1.0 over this range of scan rates, indicating that the reduction product was stable on the time scale of cyclic voltammetry. The average value of the peak potential separation, ΔE_p, was 0.063 ± 0.002 V; this value is in reasonable agreement with the 0.059 V separation expected for a one-electron reversible electrode process at the temperature of the experiment. A similar detailed study of the oxidation process at 1.22 V indicated that $E_p{}^a$ and $i_p{}^a/v^{1/2}$ were independent of v,

$i_p{}^c/i_p{}^a$ was 1.0, and ΔE_p was 0.062 ± 0.001 V over the range of scan rates described above.

Taken together, the results described above demonstrate that the reduction wave at −0.30 V and oxidation wave at 1.22 V correspond to the one-electron reversible reactions given below in eqs 2 and 3, respectively. Furthermore, neither of these

$$[(Ta_6Cl_{12})Cl_6]^{2-} + e^- \rightleftharpoons [(Ta_6Cl_{12})Cl_6]^{3-} \quad (2)$$

$$[(Ta_6Cl_{12})Cl_6]^{2-} \rightleftharpoons [(Ta_6Cl_{12})Cl_6]^- + e^- \quad (3)$$

reactions appears to be complicated by coupled homogeneous chemistry on the time scale of voltammetry. The formation of a species derived from the {Ta$_6$Cl$_{12}$}$^{5+}$ core, e.g., [(Ta$_6$Cl$_{12}$)Cl$_6$]$^-$, was unexpected. No such species was reported during electrochemical studies involving the related tertiary phosphine complexes,[9] and perusal of the literature revealed a paucity of compounds derived from this core cluster. According to Cotton's scheme,[4] the Ta−Ta bond order in this cluster is very close to $^1/_2$. We made several attempts to produce a bulk solution of this oxidized species by exhaustive CPE of a [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ solution at an applied potential, E_{app}, of 1.40 V. However, during this experiment, the platinum anode became covered with a dull orange-brown deposit that was insoluble in aqueous nitric acid and common organic solvents. A cyclic voltammogram acquired at the conclusion of the CPE

(18) Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406.

(19) Although no $E_{1/2}$ for the Fe(cp)$_2^{0/+}$ couple in 60.0−40.0 mol % AlCl$_3$−[MeEtim]Cl at 40 °C has been reported in the literature, a value of 0.260 V has been given for this couple in 60.0−40.0 mol % AlCl$_3$−1-(1-butyl)pyridinium chloride (AlCl$_3$−[Bupy]Cl) at this temperature (versus the Al(III)/Al couple in the corresponding 66.7−33.3 mol % melt).[20] The $E_{1/2}$ of the Fe(cp)$_2^{0/+}$ couple in AlCl$_3$−[MeEtim]Cl should be very close to this value because there are only minor differences in the chemical properties of these two melts.

(20) Karpinski, Z. J.; Nanjundiah, C.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 3358.
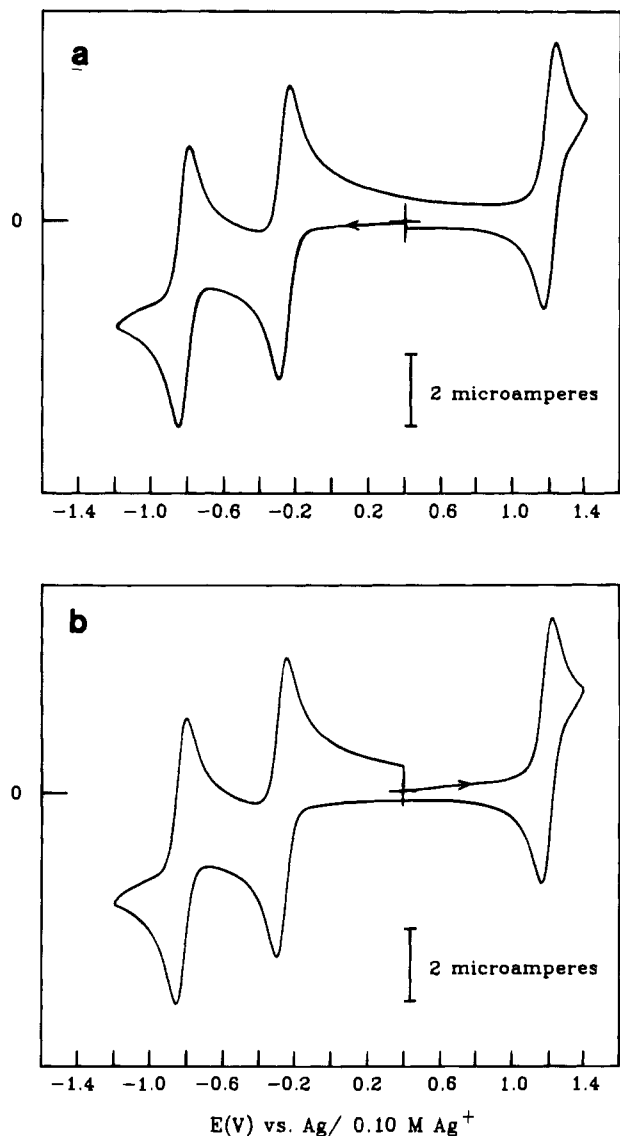
Figure 1. Cyclic voltammograms: (a) scan toward negative potentials; (b) scan toward positive potentials. The scan rates were 50 mV s^{-1}, and the initial potential for each scan was 0.40 V.

experiment indicated that no electroactive species remained in the solution. Therefore, we conclude that [(Ta$_6$Cl$_{12}$)Cl$_6$]$^-$ exhibits only transient stability under the conditions employed during this study.

In order to further explore the reduction of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ to [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-}$ and to assess the long term stability of the latter species in CH$_3$CN, solutions containing [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ were subjected to exhaustive CPE at E_{app} = -0.45 and -0.60 V. The average value of n based on the charge passed and the quantity of cluster in the solution during these experiments was 0.99 ± 0.04. The resulting solutions were bright yellow. Cyclic voltammograms of the solution in Figure 1 after reduction at E_{app} = -0.60 V as described above are shown in Figure 2. These voltammograms are very similar to those depicted in Figure 1—i.e., the same redox couples are accessible—however, the rest potential of the solution now resides between the two reduction waves at -0.30 and -0.87 V, indicating a decrease in the oxidation level of the cluster. Spectroscopic data acquired with such a reduced solution were very similar to those recorded for a solution prepared by simply dissolving [MeEtim]$_3$[(Ta$_6$Cl$_{12}$)Cl$_6$] in CH$_3$CN, indicating that [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-}$ was indeed the species produced by the electrochemical reduction of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ (Table 1).
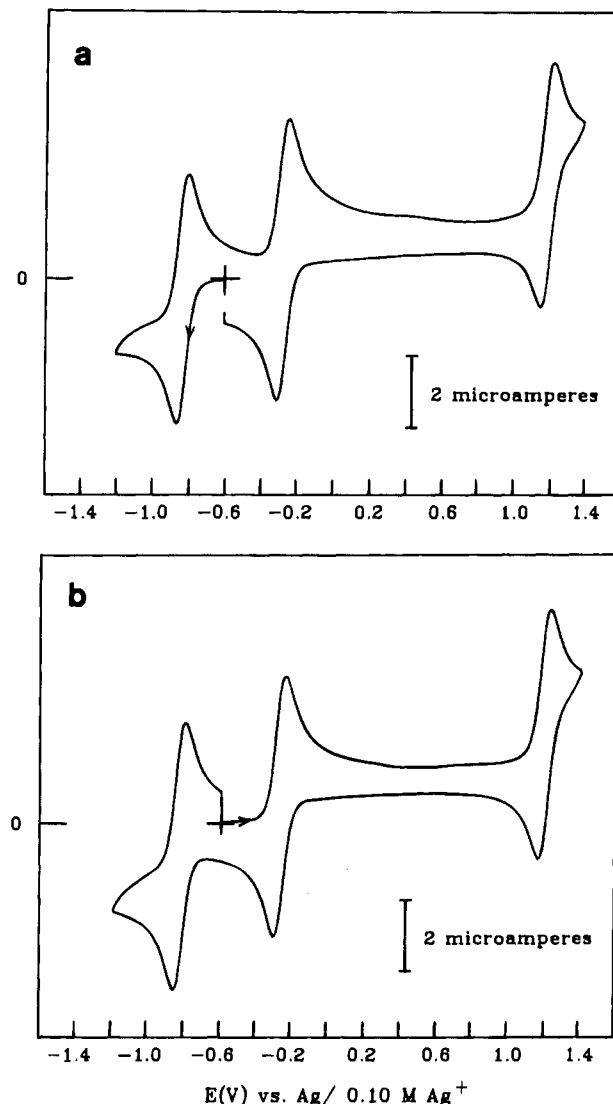

Figure 2. Cyclic voltammograms of the solution in Figure 1 at a platinum electrode after exhaustive reduction at -0.60 V: (a) scan toward negative potentials; (b) scan toward positive potentials. The scan rates were 50 mV s^{-1}, and the initial potential for each scan was -0.60 V.

A detailed cyclic voltammetric study of the reduction wave at -0.87 V was conducted with a solution of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-}$ over the same range of scan rates used to probe the oxidation and reduction of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ (*vide supra*). These experiments revealed that E_p^c and $i_p^c/v^{1/2}$ were independent of v, the average value of ΔE_p was 0.062 ± 0.001, and i_p^a/i_p^c was close to 1.0, suggesting that the reduction wave at -0.87 V corresponds to the one-electron reversible reaction shown in eq 4 and that this reaction is not complicated by coupled homogeneous chemistry on the time scale of voltammetry.

$$[(Ta_6Cl_{12})Cl_6]^{3-} + e^- \rightleftharpoons [(Ta_6Cl_{12})Cl_6]^{4-} \qquad (4)$$
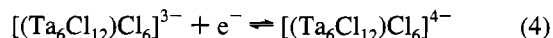
Solutions of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-}$ were subjected to several exhaustive CPE experiments at E_{app} between -1.10 and -1.40 V in an attempt to prepare a bulk solution of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$. The average value of n that resulted from these experiments was 1.08 ± 0.05, and the resulting solutions were emerald-green in color. A cyclic voltammogram of a solution reduced at E_{app} = -1.20 V is shown in Figure 3a. This voltammogram is considerably different from those shown in Figures 1 and 2. First, the oxidation peak currents for the [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-/3-}$,

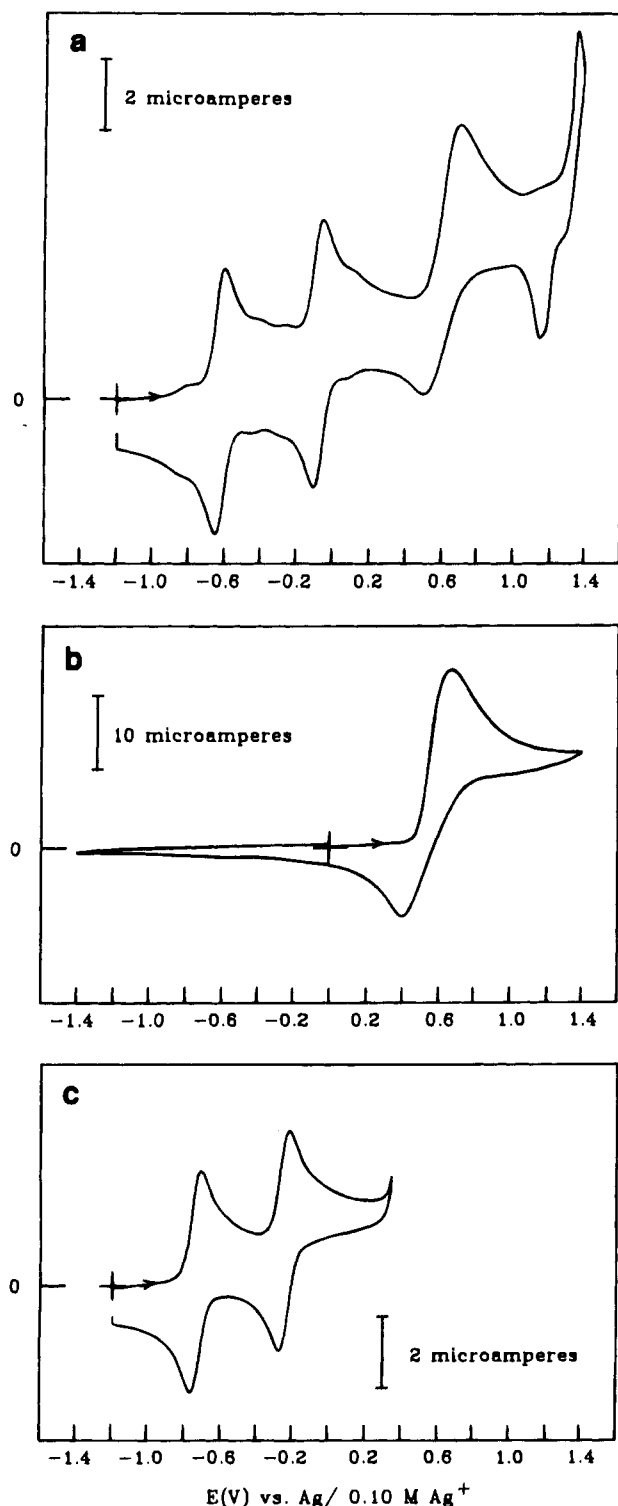**Figure 3.** Cyclic voltammograms at platinum electrodes: (a) solution described in Figure 1 after exhaustive reduction at −1.10 V (initial potential = −1.20 V); (b) 2.86 mM solution of [MeEtim]Cl in CH$_3$-CN/0.20 M [(n-Bu)$_4$N]PF$_6$ (initial potential = 0 V); (c) solution in part a after the addition of 0.53 M [MeEtim]Cl (initial potential = −1.20 V). The scan rates were 50 mV s^{-1}.

[(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-/2-}$, and [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-/-}$ electrode reactions, which appear at $E_p{}^a$ = −0.81, −0.24, and 1.22 V, respectively, in Figures 1 and 2 are barely visible in Figure 3a. Second, four new oxidation waves are evident at $E_p{}^a$ = −0.61, −0.07, 0.68, and 1.31 V. All of these waves exhibit reverse currents. These results imply that the one-electron reduction of [(Ta$_6$-Cl$_{12}$)Cl$_6$]$^{3-}$ carried out on the relatively long time scale of CPE does not produce significant amounts of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$.

Table 2. Voltammetric Analysis of Chloride Ion in Solutions of [(Ta$_6$Cl$_{12}$)Cl$_6$]^2 Reduced at − 1.10 V

current (μA)	[Cl$^-$]^a (mM)	[Ta$_6$]^b (mM)	[Cl$^-$]/[Ta$_6$]
3.89	1.02	0.857	1.19
5.15	1.32	1.08	1.22
6.63	1.68	1.29	1.30
8.19	2.05	1.99	1.03
			Av:1.2 ± 0.2^c

^{a} Concentration of chloride ion in the reduced solution. ^{b} Concentration of cluster in the original solution before electrolysis. ^{c} 95% confidence interval.

Furthermore, the oxidation wave appearing at 0.68 V is similar to one observed at a platinum electrode in a CH$_3$CN/[(n-Bu)$_4$N]-PF$_6$ solution containing only [MeEtim]Cl (Figure 3b). This wave is attributed to the oxidation of chloride ion (*vide infra*). The presence of chloride ion in the solution following the reduction of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-}$ implies that one or more of the six peripheral chloride ions coordinated to the original cluster may have been replaced by the solvent during CPE to give a complex with fewer than eighteen chlorides, e.g., [(Ta$_6$-Cl$_{12}$)Cl$_{6-x}$(CH$_3$CN)$_x$]$^{(4-x)-}$ ($x \leq 6$). This reaction appears to involve a homogeneous following chemical step coupled to the electron transfer process, i.e., an EC mechanism; however, the diminutive rate of this chemical reaction precludes its detection by cyclic voltammetry. The replacement of chloride ion by CH$_3$-CN would also account for the positive shifts in $E_p{}^a$ for the {Ta$_6$Cl$_{12}$}$^{2+/3+}$ and {Ta$_6$Cl$_{12}$}$^{3+/4+}$ redox reactions from −0.81 and −0.24 V, respectively, in Figure 1 to −0.61 and −0.07 V, respectively, in Figure 3a.

The value of x in [(Ta$_6$Cl$_{12}$)Cl$_{6-x}$(CH$_3$CN)$_x$]$^{(4-x)-}$ was estimated by measuring the current for the chloride ion oxidation wave in solutions of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ that were exhaustively reduced at E_{app} = −1.40 V. These oxidation currents were compared to a calibration curve consisting of $i_p{}^a$ versus chloride concentration that was generated by measuring the chloride ion oxidation current for CH$_3$CN/[(n-Bu)$_4$N]PF$_6$ solutions containing different amounts of [MeEtim]Cl. The results of four such experiments are given in Table 2. The ratio of the concentration of chloride ion in the electrolyzed solution to the concentration of cluster in the initial solution, represented as [Cl$^-$]/[Ta$_6$] in this table, indicates that approximately one chloride ion is displaced per hexameric cluster unit during the reduction process to give [(Ta$_6$Cl$_{12}$)Cl$_5$(CH$_3$CN)]$^{3-}$.

A large amount of [MeEtim]Cl was added to a solution of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ reduced at −1.10 V to determine if excess chloride ion would displace CH$_3$CN from the [(Ta$_6$-Cl$_{12}$)Cl$_5$(CH$_3$CN)]$^{3-}$ complex. Figure 3c shows a cyclic voltammogram of the solution in Figure 3a after the addition of sufficient [MeEtim]Cl to raise the chloride concentration to ca. 0.53 M. The addition of chloride ion, as [MeEtim]Cl, causes the oxidation waves at $E_p{}^a$ = −0.61 and −0.07 V to disappear and new waves to appear at $E_p{}^a$ = −0.71 and −0.22 V, respectively. Although the latter waves undoubtedly arise from the [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-/3-}$ and [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{3-/2-}$ electrode reactions, both exhibit small positive potential shifts relative to the corresponding waves in Figure 1. The origin of these potential shifts was revealed when a large amount of [MeEtim]Cl was added to a solution of [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ in CH$_3$CN/[(n-Bu)$_4$N]-PF$_6$. The reverse scan of a cyclic voltammogram of this solution (Figure 4, upper half) shows positive shifts in these oxidation waves similar to those seen in Figure 3c. Furthermore, a voltammogram of this solution acquired after the solution was reduced at E_{app} = −1.10 (Figure 4, lower half) is identical to that shown in Figure 3c. Thus, it may be concluded that the addition of excess chloride ion to solutions containing
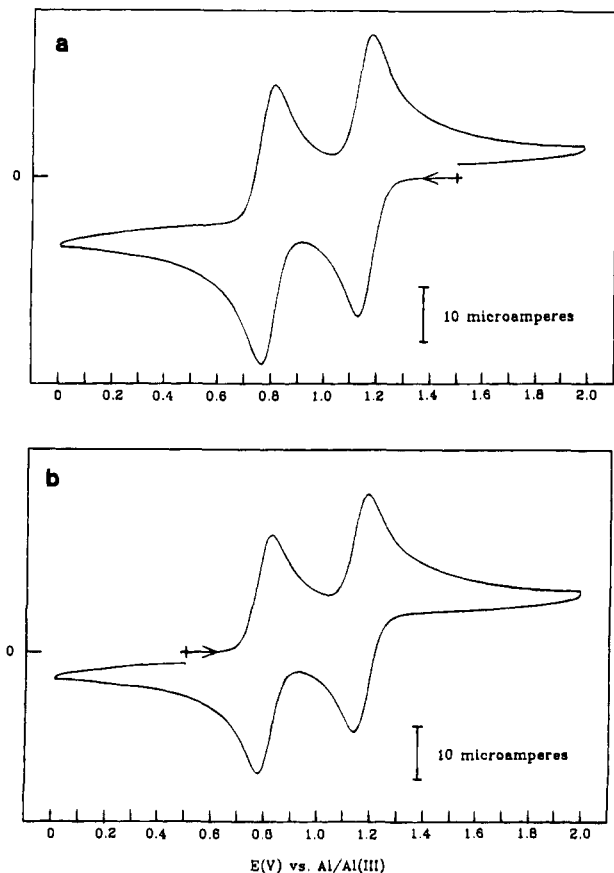
Figure 4. Cyclic voltammograms of a 1.08 mM solution of [MeEtim]2-[(Ta6Cl12)Cl6] in CH3CN/0.20 M [(n-Bu)4N]PF6 + 0.53 M [MeEtim]-Cl at a platinum electrode: (upper) before reduction (initial potential = 0.20 V); (lower) after reduction at −1.10 V (initial potential = −1.10 V). The scan rates were 50 mV s⁻¹.

Scheme 1

$(E_{1/2} = 1.19V)$

$$[(Ta_6Cl_{12})Cl_6]^{2-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(Ta_6Cl_{12})Cl_6]^-$$

red-orange   unstable

$+e^- \downarrow \uparrow -e^-$ $(E_{1/2} = -0.28$ V)

$$[(Ta_6Cl_{12})Cl_6]^{3-}$$

yellow

$+e^- \downarrow \uparrow -e^-$ $(E_{1/2} = -0.84$ V)

$+CH_3CN$
$$[(Ta_6Cl_{12})Cl_6]^{4-} \underset{-CH_3CN}{\rightleftharpoons} [(Ta_6Cl_{12})Cl_5(CH_3CN)]^{3-} + Cl^-$$

green   green

[(Ta6Cl12)Cl5(CH3CN)]³⁻ converts this complex to [(Ta6-Cl12)Cl6]⁴⁻. Furthermore, the latter species can be produced directly by reducing [(Ta6Cl12)Cl6]²⁻ (and presumably [(Ta6-Cl12)Cl6]³⁻) in a solution initially containing a large excess of chloride ion. The small potential shift that is observed after the addition of [MeEtim]Cl was attributed to electrostatic or other significant interactions between the anionic tantalum complexes and MeEtim⁺ ions. The electrochemical reactions that are associated with the various tantalum clusters in CH3-CN/[(n-Bu)4N]PF6 are summarized in Scheme 1.

Absorption spectra of [(Ta6Cl12)Cl6]⁽⁶⁻ᶻ⁾⁻ (z = 2−4) complexes are shown in Figure 5. The spectra for the z = 2 and 3 species were obtained by the successive electrochemical reduction of a dilute solution of [(Ta6Cl12)Cl6]²⁻ at E_{app} = −0.50 and −1.10 V, respectively, in CH3CN/[(n-Bu)4N]PF6 containing 0.33 M [MeEtim]Cl. A similar electrolysis experiment was conducted with a solution of [(Ta6Cl12)Cl6]²⁻ that did not contain any added [MeEtim]Cl. As expected, a cyclic voltammogram of the latter solution after reduction at −1.10 V was very similar to that shown in Figure 3a, indicating obvious corruption of

Figure 5. Electronic absorption spectra of a 2.58 × 10⁻⁴ M solution of [MeEtim]2[(Ta6Cl12)Cl6] in CH3CN/0.20 M [(n-Bu)4N]PF6 containing 0.33 M [MeEtim]Cl: (—) before reduction; (•••) after exhaustive reduction at −0.50 V; (- -) after exhaustive reduction at −1.10 V. The cell path length was 1.00 mm.

the original [(Ta6Cl12)Cl6]⁴⁻ cluster by CH3CN. Interestingly, the absorption spectrum of this solution was very similar to that recorded for a solution of [(Ta6Cl12)Cl6]⁴⁻, i.e., absorption bands for [(Ta6Cl12)Cl5(CH3CN)]³⁻ appeared at approximately the same wavelengths as found for the former, indicating that the replacement of a single terminal chloride ligand by CH3CN has very little influence on the electronic absorption spectrum of the cluster.

AlCl3−[MeEtim]Cl. The [MeEtim]2[(Ta6Cl12)Cl6] salt dissolved readily in the acidic 60−40 mol % melt to produce an orange-red colored solution. A cyclic voltammogram of such a solution at a glassy carbon electrode initiated from the rest potential at ca. 1.50 V and scanned toward more negative potentials is shown in Figure 6a. Two reduction waves at E_p^c = 1.13 and 0.76 V are evident. In addition, oxidation waves associated with these reduction waves are located at E_p^a = 1.19 and 0.82 V, respectively, on the reverse scan. No other voltammetric waves that could be attributed to the tantalum cluster solute were detected within the potential window of the molten salt. The general appearance of this cyclic voltammogram, i.e., two reduction waves with reverse currents, is very similar to that seen in the −1.20 to 0 V potential region of Figure 1 and in a voltammogram of the related phosphine complex (Figure 1, ref 9), suggesting that the {Ta6Cl12}⁴⁺ core cluster was preserved upon dissolution of the [MeEtim]2[(Ta6Cl12)Cl6] salt in acidic AlCl3−[MeEtim]Cl.

A detailed cyclic voltammetric investigation of the first reduction wave and associated oxidation wave in Figure 6a was carried out over the range of scan rates from 0.010 to 0.200 V s⁻¹; E_p^c and $i_p^c/v^{1/2}$ were found to be independent of v, i_p^a/i_p^c was 1.0, and the average value of ΔE_p was 0.061 ± 0.001 V. The latter result is in excellent agreement with the 0.062 V peak potential separation expected for a one-electron reversible electrode reaction at 40 °C. Thus, the first reduction process corresponds to a reversible, uncomplicated, one-electron reaction in which a species with the {Ta6Cl12}⁴⁺ core is converted to one with the {Ta6Cl12}³⁺ core. This reaction is similar to that found in CH3CN at $E_{1/2}$ = −0.27 V (Figure 1).

In order to assess the stability of the various reduced cluster species in the melt, a solution of [MeEtim]2[(Ta6Cl12)Cl6] in 60.0−40.0 mol % melt was subjected to exhaustive CPE at E_{app} = 0.50 V. The resulting solution was blue-green in color and was stable indefinitely, provided that the solution was protected from moisture and oxygen. A cyclic voltammogram of the

Figure 6. Cyclic voltammogram of a 11.6 mM solution of [MeEtim]$_2$-[(Ta$_6$Cl$_{12}$)Cl$_6$] in 60.0—40.0 mol % AlCl$_3$—[MeEtim]Cl at a glassy carbon electrode: (a) before reduction (initial potential = 1.50 V); (b) after exhaustive reduction at 0.50 V (initial potential = 0.50 V). The scan rates were 50 mV s^{-1}.
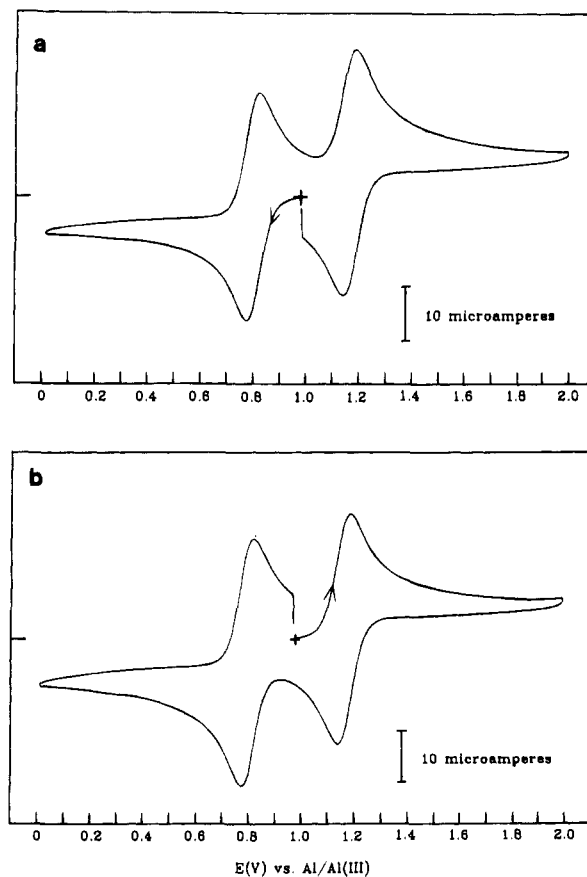
Figure 7. Cyclic voltammograms of the solution in Figure 6b at a glassy carbon electrode after exhaustive oxidation at 0.98 V: (a) scan toward negative potentials; (b) scan toward positive potentials. The scan rates were 50 mV s^{-1}, and the initial potential for both scans was 0.98 V.

reduced solution is shown in Figure 6b; the same redox processes that were observed in the solution before reduction are accessible after reduction, and no new voltammetric waves are evident in the reduced solution. However, the rest potential of the reduced solution is now located at 0.50 V.

A detailed cyclic voltammetric analysis of the oxidation wave at $E_p^a = 0.82$ V and its associated reduction wave revealed that E_p^a and $i_p^a/v^{1/2}$ were independent of v, i_p^c/i_p^a was 1.0, and the average value of ΔE_p was 0.060 ± 0.002 V over the same range of scan rates described above. Taken together, these results suggest that the oxidation wave at $E_p^a = 0.82$ V corresponds to the one-electron, reversible oxidation of a species with the {Ta$_6$-Cl$_{12}$}$^{2+}$ core to a species with the {Ta$_6$Cl$_{12}$}$^{3+}$ core. This reaction is analogous to that found at $E_{1/2} = -0.84$ V in CH$_3$-CN, and it does not appear to be complicated by coupled homogeneous chemistry on the voltammetric time scale. Exhaustive controlled-potential oxidation of this same solution at $E_{app} = 0.98$ V produced a lime-green solution. Cyclic voltammograms of this solution are shown in Figure 7, and they indicate that the solution now contains a species with the {Ta$_6$-Cl$_{12}$}$^{3+}$ core cluster. A detailed voltammetric investigation of this species similar to that described above revealed that it can be oxidized and reduced in one-electron reversible reactions to produce products that are stable on the voltammetric time scale. Exhaustive bulk oxidation of this solution at $E_{app} = 1.50$ V produced a solution with voltammetric characteristics identical in all respects to those of the original solution prepared by dissolving the [MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$] salt (*vide supra*).

Absorption spectra of dilute solutions of [MeEtim]$_2$[(Ta$_6$Cl$_{12}$)-Cl$_6$] in 60.0—40.0 mol % melt recorded before and after the
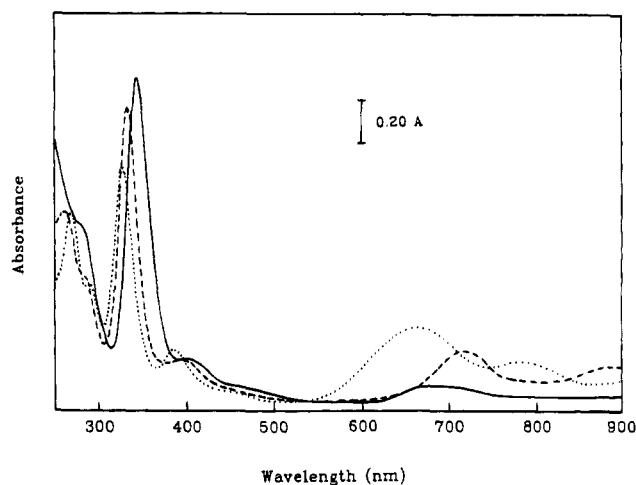
Figure 8. Electronic absorption spectra of 8.11 × 10^{-4} M solutions of [MeEtim]$_2$[(Ta$_6$Cl$_{12}$)Cl$_6$] in 60.0—40.0 mol % AlCl$_3$—[MeEtim]Cl: (—) before reduction; (- -) after exhaustive reduction at 0.98 V; (•••) after exhaustive reduction at 0.50 V. The cell path lengths were 1.00 mm.

successive reduction of this solution at $E_{app} = 0.98$ and 0.50 V, respectively, are shown in Figure 8. Absorption maxima and molar absorptivities taken from these spectra are collected in Table 1. The spectra in Figure 8 show considerable qualitative similarities to those of the corresponding anionic clusters in CH$_3$-CN (Figure 5), confirming that the core cluster is retained in the very Lewis acidic AlCl$_3$—[MeEtim]Cl melt. However, the absorption bands for the clusters in acidic melt are shifted toward
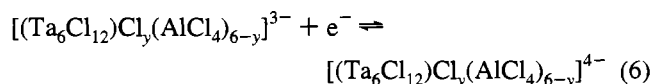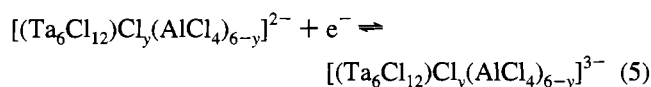
Table 3. Summary of Electrochemical Data for Hexameric Tantalum Clusters

electroactive species	redox reaction	solvent	$E_{1/2}$ (V)	$10^7 D$ (cm² s⁻¹)	$10^{11} D/T$ (g cm s⁻² K⁻¹)
[(Ta₆Cl₁₂)Cl₆]²⁻	{Ta₆Cl₁₂}⁴⁺/⁵⁺	CH₃CN + 0.20 M [(n-Bu)₄N]PF₆	1.192 (1.155)[a]	89 ± 6	11 ± 1
[(Ta₆Cl₁₂)Cl₆]²⁻	{Ta₆Cl₁₂}⁴⁺/³⁺	CH₃CN + 0.20 M [(n-Bu)₄N]PF₆	−0.274 (−0.311)	88 ± 2	11 ± 1
[(Ta₆Cl₁₂)Cl₆]³⁻ [b]	{Ta₆Cl₁₂}³⁺/⁴⁺	CH₃CN + 0.20 M [(n-Bu)₄N]PF₆	−0.279 (−0.316)	79 ± 2	9.8 ± 0.3
[(Ta₆Cl₁₂)Cl₆]³⁻ [b]	{Ta₆Cl₁₂}³⁺/²⁺	CH₃CN + 0.20 M [(n-Bu)₄N]PF₆	−0.835 (−0.872)	82 ± 6	10 ± 1
[(Ta₆Cl₁₂)Cl₆]²⁻	{Ta₆Cl₁₂}⁴⁺/³⁺	CH₃CN + 0.20 M [(n-Bu)₄N]PF₆ + 0.50 M [MeEtim]Cl	−0.255	61	
[(Ta₆Cl₁₂)Cl₆]³⁻ [c]	{Ta₆Cl₁₂}³⁺/⁴⁺	CH₃CN + 0.20 M [(n-Bu)₄N]PF₆ + 0.50 M [MeEtim]Cl	−0.249	48	
[(Ta₆Cl₁₂)Cl₆]³⁻ [c]	{Ta₆Cl₁₂}³⁺/²⁺	CH₃CN + 0.20 M [(n-Bu)₄N]PF₆ + 0.50 M [MeEtim]Cl	−0.736	47	
ferrocene	Fe(cp)₂⁰/⁺	CH₃CN + 0.20 M [(n-Bu)₄N]PF₆	0.037	240	
[(Ta₆Cl₁₂)Clᵧ(AlCl₄)₆₋ᵧ]²⁻	{Ta₆Cl₁₂}⁴⁺/³⁺	60−40 mol % AlCl₃−[MeEtim]Cl	1.160 (0.900)	2.9 ± 0.3	10 ± 1
[(Ta₆Cl₁₂)Clᵧ(AlCl₄)₆₋ᵧ]³⁻ [d]	{Ta₆Cl₁₂}³⁺/⁴⁺	60−40 mol % AlCl₃−[MeEtim]Cl	1.158 (0.898)	2.6 ± 0.2	8.9 ± 0.8
[(Ta₆Cl₁₂)Clᵧ(AlCl₄)₆₋ᵧ]³⁻ [d]	{Ta₆Cl₁₂}³⁺/²⁺	60−40 mol % AlCl₃−[MeEtim]Cl	0.794 (0.534)	2.6 ± 0.2	8.9 ± 0.8
[(Ta₆Cl₁₂)Clᵧ(AlCl₄)₆₋ᵧ]⁴⁻ [e]	{Ta₆Cl₁₂}²⁺/³⁺	60−40 mol % AlCl₃−[MeEtim]Cl	0.791 (0.531)	2.3 ± 0.2	7.8 ± 0.6
ferrocene	Fe(cp)₂⁰/⁺	60−40 mol % AlCl₃−[Bupy]Cl	0.260		

[a] Potential versus Fe(cp)₂⁰/⁺. [b] After reduction of [MeEtim]₂[(Ta₆Cl₁₂)Cl₆] at −0.60 V vs Ag/0.10 M Ag⁺. [c] After reduction of [MeEtim]₂[(Ta₆Cl₁₂)Cl₆] at −0.50 V vs Ag/0.10 M Ag⁺. [d] After reduction of [MeEtim]₂[(Ta₆Cl₁₂)Cl₆] at 0.98 V vs Al/Al(III). [e] After reduction of [MeEtim]₂[(Ta₆Cl₁₂)Cl₆] at 0.50 V vs Al/Al(III).

shorter wavelengths relative to the corresponding bands for the anionic clusters in CH₃CN.

Although species containing the {Ta₆Cl₁₂}$^{p+}$ (p = 2, 3, and 4) core clusters are stable in the acidic AlCl₃−[MeEtim]Cl molten salt, the coordination of these clusters is only speculative. EXAFS results reported by Dent et al.[21] show that simple metal ions such as cobalt(II) and nickel(II) are weakly coordinated by [AlCl₄]⁻ in acidic AlCl₃-[MeEtim]Cl. Intersolvent comparisons of the tantalum cluster redox potentials in the two solvents used in this study were made by referencing these potentials to the $E_{1/2}$ of the ferrocene/ferrocenium (Fe(cp)₂⁰/⁺) couple.[19] These $E_{1/2}$ values are given in parentheses in the fourth column of Table 3. Comparison of these potentials reveals that the {Ta₆Cl₁₂}⁴⁺/³⁺ and {Ta₆Cl₁₂}³⁺/²⁺ redox reactions in acidic AlCl₃-[MeEtim]Cl are located more than one volt positive of the corresponding reactions in CH₃CN/[(n-Bu)₄N]PF₆. This suggests that the majority, if not all, of the six peripheral chloride ions on the anionic chloride clusters are replaced by [AlCl₄]⁻ upon dissolution in the melt. Such a substitution explains the large positive potential shifts found here. Thus, the {Ta₆Cl₁₂}⁴⁺/³⁺ and {Ta₆Cl₁₂}³⁺/²⁺ redox reactions in acidic AlCl₃−[MeEtim]-Cl most likely correspond to

$$[(Ta_6Cl_{12})Cl_y(AlCl_4)_{6-y}]^{2-} + e^- \rightleftharpoons$$
$$[(Ta_6Cl_{12})Cl_y(AlCl_4)_{6-y}]^{3-} \quad (5)$$

$$[(Ta_6Cl_{12})Cl_y(AlCl_4)_{6-y}]^{3-} + e^- \rightleftharpoons$$
$$[(Ta_6Cl_{12})Cl_y(AlCl_4)_{6-y}]^{4-} \quad (6)$$

where $y \leq 6$. Similar conclusions were reached during an investigation of the electrochemistry of the related niobium clusters.[5] In this study, large positive shifts in the $E_{1/2}$ of the {Nb₆Cl₁₂}⁴⁺/³⁺ and {Nb₆Cl₁₂}³⁺/²⁺ redox reactions were observed on going from basic to acidic AlCl₃-[MeEtim]Cl.

Diffusion Coefficients. Diffusion coefficients, D, and Stokes−Einstein products, $\eta D/T$, where η is the absolute viscosity of the solvent and T is the absolute temperature, are presented in Table 3. Diffusion coefficients measured in CH₃CN/[(n-Bu)₄N]-PF₆ were calculated from cyclic voltammetric data, whereas those measured in AlCl₃−MeEtimCl are the average results from cyclic and RDE voltammetry and chronoamperometry. The Stokes−Einstein product is inversely proportional to the solvodynamic radius, r_{solv}, of the diffusing entity through the well-known Stokes-Einstein equation:

$$\eta D/T = k/C\pi r_{solv} \quad (7)$$

The parameters k and C that appear in eq 7 are the Boltzmann constant and a numerical constant that is customarily assigned a value of 6, respectively. The absolute viscosity of the CH₃-CN/0.20 M [(n-Bu)₄N]PF₆ mixtures used in this study was calculated from the measured kinematic viscosity and density of this solution and found to be 3.66 × 10⁻³ g cm⁻¹ s⁻¹ at 23 °C. Viscosity data for the 60−40 mol % AlCl₃−[MeEtim]Cl melt were taken from the article by Fannin et al.[22] Three conclusions can be reached from the data in this table. First, there is no statistical difference in r_{solv} for the [(Ta₆Cl₁₂)Cl₆]$^{(6-z)-}$ (z = 3 and 4) clusters in CH₃CN. Second, the solvated radii of the [(Ta₆Cl₁₂)Cl₆]$^{(6-z)-}$ clusters in CH₃CN are nearly the same as those measured for the corresponding [(Nb₆Cl₁₂)Cl₆]$^{(6-z)-}$ clusters in basic AlCl₃-[MeEtim]Cl.[5] Third, r_{solv} for the [(Ta₆Cl₁₂)Clᵧ(AlCl₄)₆₋ᵧ]$^{(6-z)-}$ (z = 2 and 3) clusters in acidic AlCl₃−[MeEtim]Cl is indistinguishable from that of the related niobium species in this same solvent.[5]

(21) Dent, A. J.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Chem. Commun.* **1990**, 315.

(22) Fannin, A. A.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. *J. Phys. Chem.* **1984**, *88*, 2614.