

pair with a potassium biphthalate buffer of pH 4.00 in their pH measurements as compared to the multipoint standardization used in the present study. It is known that in practical pH measurements the potential-pH slope of glass-reference electrode pairs mostly is less than the theoretical slope.<sup>37,38</sup> Consequently, the pH measured on the basis of a single-point calibration will systematically differ from the actual pH, the deviation being greater, the greater the difference between the

actual pH and the calibration pH.<sup>38,39</sup> On this basis and in view of the rather severe restrictions imposed on the analytical data by the least-squares adjustment, the estimates of the thermodynamic solubility product of  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  and of the association constants of  $\text{MgH}_2\text{PO}_4^+$  and  $\text{MgHPO}_4$  obtained in the present study form a consistent and more reliable set of constants.

Registry No.  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ , 7782-75-4.

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## Electrochemical Study of Tungsten Chloro Complex Chemistry in the Basic Aluminum Chloride-1-Methyl-3-ethylimidazolium Chloride Ionic Liquid

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Absorption spectroscopy indicated that the addition of  $\text{WCl}_6$  or  $\text{KWCl}_6$  to the basic aluminum chloride-1-methyl-3-ethylimidazolium chloride ionic liquid produced the tungsten(V) chloro complex  $[\text{WCl}_6]^-$ . This species can be reduced to  $[\text{WCl}_6]^{2-}$  and  $[\text{WCl}_6]^{3-}$  via two consecutive, reversible, one-electron reduction processes with voltammetric half-wave potentials of 0.45 and -0.80 V, respectively, referenced to aluminum in 66.7:33.3 mol % melt. The metal-bonded tungsten(III) dimer  $[\text{W}_2\text{Cl}_9]^{3-}$  exhibited two one-electron voltammetric oxidation waves with half-wave potentials of -0.07 and 0.43 V, respectively. The first wave corresponded to the formation of  $[\text{W}_2\text{Cl}_9]^{2-}$  and was reversible and uncomplicated on the voltammetric time interval. The second wave did not exhibit a reverse current. However, the oxidation of  $[\text{W}_2\text{Cl}_9]^{3-}$  consumed two electrons per mole of  $[\text{W}_2\text{Cl}_9]^{3-}$  on the time interval encompassed by controlled-potential coulometry and  $[\text{WCl}_6]^{2-}$  was the sole product. This suggested that coulometric oxidation of  $[\text{W}_2\text{Cl}_9]^{3-}$  follows an ECE pathway with the following steps: (1) one-electron oxidation of  $[\text{W}_2\text{Cl}_9]^{3-}$  to  $[\text{W}_2\text{Cl}_9]^{2-}$ , (2) slow disproportionation of  $[\text{W}_2\text{Cl}_9]^{2-}$  to  $[\text{WCl}_6]^{2-}$  and a tungsten(III) complex, and (3) one-electron oxidation of the tungsten(III) complex to  $[\text{WCl}_6]^{2-}$ . The Stokes-Einstein equation was applicable to  $[\text{WCl}_6]^-$ ,  $[\text{WCl}_6]^{2-}$ , and  $[\text{W}_2\text{Cl}_9]^{3-}$  over a large range of melt composition. Diffusion coefficients for these species in 44.4 mol % melt at 40.0 °C were  $(2.8 \pm 0.2) \times 10^{-7}$ ,  $(2.2 \pm 0.1) \times 10^{-7}$ , and  $(1.5 \pm 0.1) \times 10^{-7}$   $\text{cm}^2 \text{s}^{-1}$ , respectively. Close agreement was obtained between experimental solvodynamic and calculated structural radii for both  $[\text{WCl}_6]^-$  and  $[\text{WCl}_6]^{2-}$ , which suggested that these species were essentially unsolvated in the melt.

### Introduction

Aluminum chloride can be combined with certain organic salts to produce ionic liquids at room temperature. Familiar examples of such liquids are mixtures of aluminum chloride with 1-*n*-butylpyridinium chloride (BPC) or 1-methyl-3-ethylimidazolium chloride (MEIC).<sup>1,2</sup> Both systems have been found to be good solvents for electrochemistry and spectroscopy. The Lewis acid-base properties of these ionic liquids can be varied by adjusting the ratio of  $\text{AlCl}_3$  to organic salt. Melts in which the apparent mole fraction of  $\text{AlCl}_3$  exceeds 0.5 are acidic, owing to the presence of the heptachloroaluminate ion, which is a chloride ion acceptor. Those melts with an  $\text{AlCl}_3$  mole fraction less than 0.5 are basic, since they contain uncomplexed chloride ion.

The results obtained during previous studies indicate that transition-metal ions form very stable anionic chloro complexes in basic  $\text{AlCl}_3$ -BPC or basic  $\text{AlCl}_3$ -MEIC.<sup>3-11</sup> Tetrahedral

$[\text{MCl}_4]^{n-4}$  chloro complex anions were found for most dipositive and tripositive 3d ions in these melts.<sup>3-8</sup> A series of  $[\text{MCl}_p]^{1-p}$  complexes with  $2 \leq p \leq 4$  were detected for copper(I)<sup>8</sup> and silver(I).<sup>9</sup> Titanium(IV), octahedrally complexed as  $[\text{TiCl}_6]^{2-}$ , was found to exist in equilibrium with an oxychloro complex,  $[\text{TiOCl}_4]^{2-}$ , when oxide ion was introduced into the melt by dissolution of  $\text{Li}_2\text{CO}_3$ .<sup>10</sup> Basic  $\text{AlCl}_3$ -MEIC was found to be a useful solvent for stabilizing the  $[\text{MoCl}_6]^{2-}$  ion, which had not been studied in solution previously.<sup>11</sup>

Several studies have been concerned with the chemistry of tungsten chloro complex solutes in alkali-metal chloride based chloroaluminate melts,<sup>12-14</sup> molten alkali-metal chlorides,<sup>15-17</sup> and conventional aprotic solvents.<sup>18,19</sup> Marshall and Yntema<sup>12</sup> examined the deposition of tungsten metal from fused Al-

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Table I. Voltammetric Data for Tungsten Chloro Complexes in 44.4 mol % AlCl<sub>3</sub>-MEIC Melt

scan rate, $\nu$ , V s <sup>-1</sup>	$\Delta E_p$ , V			$i_p^a/i_p^c$			$10^5 i_p/\nu^{1/2}$ , A s <sup>-1/2</sup>		
	[WCl <sub>6</sub> ] <sup>-a</sup>	[WCl <sub>6</sub> ] <sup>2--b</sup>	[W <sub>2</sub> Cl <sub>9</sub> ] <sup>3--c</sup>	[WCl <sub>6</sub> ] <sup>-</sup>	[WCl <sub>6</sub> ] <sup>2--</sup>	[W <sub>2</sub> Cl <sub>9</sub> ] <sup>3--d</sup>	[WCl <sub>6</sub> ] <sup>-</sup>	[WCl <sub>6</sub> ] <sup>2--</sup>	[W <sub>2</sub> Cl <sub>9</sub> ] <sup>3--</sup>
0.01	0.065	0.067	0.063	1.1	1.1	1.0	6.1	5.8	3.4
0.02	0.065	0.069	0.064	1.1	1.1	1.0	6.0	5.8	3.3
0.05	0.065	0.070	0.066	1.1	1.1	1.0	6.0	5.7	3.3
0.10	0.068	0.074	0.068	1.1	1.1	1.1	6.2	5.7	3.3
0.20	0.072	0.073	0.071	1.1	1.1	1.1	6.0	5.6	3.3
0.50	0.063	0.071	0.071	1.1	1.1	1.1	6.0	5.4	3.2
1.00	0.069	0.080	0.074	1.2	1.1	1.1	6.1	5.5	3.2

<sup>a</sup> Reduction of  $5.81 \times 10^{-3}$  M [WCl<sub>6</sub>]<sup>-</sup>. <sup>b</sup> Reduction of  $6.92 \times 10^{-3}$  M [WCl<sub>6</sub>]<sup>2--</sup>. <sup>c</sup> Oxidation of  $4.77 \times 10^{-3}$  M [W<sub>2</sub>Cl<sub>9</sub>]<sup>3--</sup>. <sup>d</sup>  $i_p^c/i_p^a$ .

Cl<sub>3</sub>-NaCl containing K<sub>3</sub>W<sub>2</sub>Cl<sub>9</sub>. The electrochemistry of several tungsten solutes, notably WCl<sub>6</sub>, [W<sub>6</sub>Cl<sub>8</sub>]Cl<sub>4</sub>, KWCl<sub>6</sub>, K<sub>2</sub>WCl<sub>6</sub>, and K<sub>3</sub>W<sub>2</sub>Cl<sub>9</sub>, was examined in molten AlCl<sub>3</sub>-NaCl, but the bulk of this study was undertaken in acidic melt.<sup>13</sup> Dorman and McCarley<sup>14</sup> synthesized [W<sub>6</sub>Cl<sub>8</sub>]Cl<sub>4</sub> by reduction of WCl<sub>6</sub> with aluminum metal in acidic AlCl<sub>3</sub>-NaCl melt. The formal potential of the W(II)/W(0) couple has been determined in molten LiCl-KCl.<sup>15</sup> Some aspects of tungsten electrochemistry have been examined in molten LiCl-KCl.<sup>16,17</sup> Mayer and Brown<sup>18</sup> obtained a one-electron reversible reduction of tungsten(VI) in dimethylformamide. The reduction of [WCl<sub>6</sub>]<sup>-</sup> and [WCl<sub>6</sub>]<sup>2--</sup> has been studied in acetonitrile.<sup>19</sup> No study of tungsten solutes in room-temperature chloro-aluminate melts has been reported.

In the present investigation the electrochemistry of WCl<sub>6</sub>, KWCl<sub>6</sub>, K<sub>2</sub>WCl<sub>6</sub>, and K<sub>3</sub>W<sub>2</sub>Cl<sub>9</sub> was examined in basic AlCl<sub>3</sub>-MEIC melt. Techniques used for this study include cyclic voltammetry, rotating-disk electrode voltammetry, controlled-potential coulometry, and absorption spectroscopy.

### Experimental Section

**Apparatus.** The drybox system and electrochemical instrumentation used for this study were identical with those employed previously.<sup>9</sup> The procedure for monitoring the moisture and oxygen content of this drybox has been described.<sup>5</sup>

A glassy-carbon-disk electrode (area 0.07 cm<sup>2</sup>), constructed according to the procedure given by Phillips et al.,<sup>20</sup> was used as the working electrode during voltammetric experiments. The cell used for these experiments consisted of a Pyrex cup with a tapered bottom, fitted with a Teflon lid. The reference electrode was an aluminum-wire spiral (Alfa, m5N) immersed in 66.7:33.3 mol % AlCl<sub>3</sub>-MEIC melt. This melt, together with the aluminum wire, was placed in a Pyrex tube that had a fine-porosity fritted disk sealed in one end. This tube was inserted into the bulk melt through a hole provided in the cell top. The counterelectrode was a molybdenum-wire spiral. It was isolated from the bulk melt in a similar fashion. A small glassy-carbon crucible served as the working electrode during controlled-potential coulometry experiments.

The cell was thermostated in a furnace constructed from an aluminum block heated by means of a Vulcan cartridge heater. The heater was controlled by using an ACE Glass 12105 proportional temperature controller equipped with a platinum temperature sensor. All electrochemical measurements were performed at  $40.0 \pm 0.2$  °C. Absorption spectra were recorded at room temperature in 1.0-cm quartz cells fitted with airtight Teflon caps with use of a Perkin-Elmer Hitachi 200 UV-vis spectrophotometer.

**Chemicals.** The procedures used for purification of AlCl<sub>3</sub> by sublimation, synthesis of MEIC, and preparation of the AlCl<sub>3</sub>-MEIC melt were similar to those described in previous publications.<sup>5,21</sup> Tungsten(VI) chloride, WCl<sub>6</sub> (Alfa Ventron, 99%, resublimed), was purified further by sublimation through a thermal gradient to remove any oxychloro contaminants. Potassium hexachlorotungstate(V), KWCl<sub>6</sub>, was prepared from WCl<sub>6</sub> and KI according to the procedure recommended by Dickinson et al.<sup>22</sup> Potassium hexachloro-

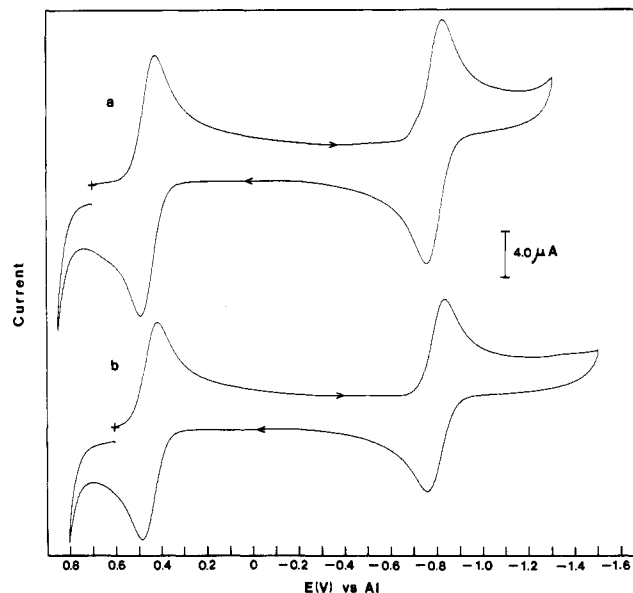


Figure 1. Cyclic voltammograms at a glassy-carbon electrode in 44.4 mol % AlCl<sub>3</sub>-MEIC at 40.0 °C: (a)  $7.0 \times 10^{-3}$  M in WCl<sub>6</sub>; (b)  $5.8 \times 10^{-3}$  M in KWCl<sub>6</sub>. Sweep rates were 0.020 V s<sup>-1</sup>.

tungstate(IV), K<sub>2</sub>WCl<sub>6</sub>, was synthesized according to the method of Kennedy and Peacock.<sup>23</sup> K<sub>3</sub>W<sub>2</sub>Cl<sub>9</sub> was prepared by using a modified version of the method proposed by Laudise and Young.<sup>24</sup> The modification involved removal of the tin salts by filtration followed by precipitation of the tungsten salt with absolute ethanol as suggested by Saillant et al.<sup>25</sup>

The oxide content of the AlCl<sub>3</sub>-MEIC melt used in this study was determined by using pulse polarography at a slowly rotating glassy-carbon electrode (GCRDE) according to the procedure developed by Osteryoung and co-workers.<sup>26</sup> Melts that contained more than 5 ppm of oxide were discarded. For conciseness, the melt compositions specified throughout this paper are expressed in terms of the apparent mole percent (mol %) of AlCl<sub>3</sub> in each AlCl<sub>3</sub>-MEIC melt.

All potentials in this paper are reported vs. an aluminum wire immersed in the nominal 66.7 mol % AlCl<sub>3</sub>-MEIC melt. It should be noted that these potentials are somewhat approximate, since it was not always possible to reproduce exactly the melt composition in the reference electrode compartment. As pointed out previously,<sup>5</sup> small errors in the reference melt composition can often lead to nonnegligible errors in the reported potentials.

### Results and Discussion

**WCl<sub>6</sub> and KWCl<sub>6</sub>.** The addition of either WCl<sub>6</sub> or KWCl<sub>6</sub> to basic AlCl<sub>3</sub>-MEIC melt resulted in a canary yellow solution. However, both solutions turned green after standing for several days. Cyclic voltammograms of fresh solutions of WCl<sub>6</sub> and KWCl<sub>6</sub> at a glassy-carbon electrode in 44.4 mol % melt are

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Table II. Voltammetric Data for Tungsten Chloro Complexes at Different Melt Compositions

mol % AlCl <sub>3</sub>	pCl	$E_p$ , V			$E_{1/2}$ , <sup>a</sup> V			$10^3 \eta D$ , <sup>b</sup> g cm s <sup>-2</sup>		
		[WCl <sub>6</sub> ] <sup>-c</sup>	[WCl <sub>6</sub> ] <sup>2-</sup> c	[W <sub>2</sub> Cl <sub>9</sub> ] <sup>3-</sup> d	[WCl <sub>6</sub> ] <sup>-</sup>	[WCl <sub>6</sub> ] <sup>2-</sup>	[W <sub>2</sub> Cl <sub>9</sub> ] <sup>3-</sup>	[WCl <sub>6</sub> ] <sup>-</sup>	[WCl <sub>6</sub> ] <sup>2-</sup>	[W <sub>2</sub> Cl <sub>9</sub> ] <sup>3-</sup>
49.5	1.043	0.422	-0.827	-0.029	0.455	-0.792	-0.062	7.1	5.2	3.2
49.0	0.740	0.420			0.453			6.9		
48.9	0.712			-0.034			-0.066			3.1
48.5	0.577	0.418			0.451			6.7		
48.3	0.524		-0.830	-0.036		-0.794	-0.068		5.1	3.0
48.0	0.452	0.418			0.451			6.7		
47.7	0.401			-0.037			-0.069			3.0
47.5	0.366	0.418			0.450			6.7		
47.2	0.313		-0.833	-0.041		-0.797	-0.073		5.0	2.9
45.7	0.146	0.414			0.446			6.5		
45.1	0.092		-0.838	-0.048		-0.803	-0.080		4.8	2.9
44.1	0.022		-0.841			-0.806			4.7	
44.0	0.017	0.405			0.437			6.3		
43.2	-0.027			-0.052			-0.085			2.8
43.1	-0.033		-0.846			-0.810				

<sup>a</sup> Estimated from  $(E_p^a + E_p^c)/2$  at a scan rate of 50 mV s<sup>-1</sup>. <sup>b</sup> Calculated from GCRDE data. <sup>c</sup> Reduction. <sup>d</sup> Oxidation.

Table III. Absorption Spectroscopic Data for Tungsten Chloro Complex Anions

solute	solvent	$\lambda_{max}$ , nm ( $\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup> )	ref
WCl <sub>6</sub>	44.4 mol % AlCl <sub>3</sub> -MEIC	275, <sup>a</sup> 299 (~1.5 × 10 <sup>4</sup> ), 347 (~8 × 10 <sup>3</sup> ), 390 <sup>a</sup>	this work
KWCl <sub>6</sub>	44.4 mol % AlCl <sub>3</sub> -MEIC	275, <sup>a</sup> 298 (~1.3 × 10 <sup>4</sup> ), 350 (~7 × 10 <sup>3</sup> ), 390 <sup>a</sup>	this work
KWCl <sub>6</sub>	CH <sub>3</sub> CN	246 (7.5 × 10 <sup>3</sup> ), ~275, <sup>a</sup> 297 (1.2 × 10 <sup>4</sup> ), 347 (7.0 × 10 <sup>3</sup> ), ~390 <sup>a</sup>	this work
RWCl <sub>6</sub> <sup>b</sup>	CH <sub>3</sub> CN	242 (4.3 × 10 <sup>3</sup> ), 270, <sup>a</sup> 297 (1.5 × 10 <sup>4</sup> ), 345 (1.1 × 10 <sup>4</sup> ), 380 (2.6 × 10 <sup>3</sup> ), 429 (4 × 10 <sup>2</sup> )	29
[WCl <sub>6</sub> ] <sup>2-</sup> c	44.4 mol % AlCl <sub>3</sub> -MEIC	287 (7.9 × 10 <sup>3</sup> ), 308, <sup>a</sup> 350 <sup>a</sup>	this work
K <sub>2</sub> WCl <sub>6</sub>	44.4 mol % AlCl <sub>3</sub> -MEIC	287 (7.7 × 10 <sup>3</sup> ), 308, <sup>a</sup> 350 <sup>a</sup>	this work
K <sub>2</sub> WCl <sub>6</sub>	CH <sub>3</sub> CN	237, <sup>a</sup> 249 (1.5 × 10 <sup>4</sup> ), 287 (7.0 × 10 <sup>3</sup> ), ~307, <sup>a</sup> ~342 <sup>a</sup>	this work
K <sub>2</sub> WCl <sub>6</sub>	mull	233, 259, 285, 314	30
K <sub>3</sub> W <sub>2</sub> Cl <sub>9</sub>	44.4 mol % AlCl <sub>3</sub> -MEIC	460 (4.0 × 10 <sup>3</sup> ), 626 (~70), 764 (~35)	this work
	12 M HCl	456 (3.5 × 10 <sup>3</sup> ), 628 (~60), 770 (~25)	this work
	12 M HCl	380, <sup>a</sup> 457 (4.7 × 10 <sup>3</sup> ), 629 (160), 758 (50)	25

<sup>a</sup> Shoulder. <sup>b</sup> R = Et<sub>4</sub>N. <sup>c</sup> Electrolytic reduction of [WCl<sub>6</sub>]<sup>-</sup>.

shown in Figure 1. These voltammograms are very similar, and both exhibit two major redox processes with reduction peak potentials,  $E_p^c$ , at about 0.42 and -0.83 V. (The oxidation current that occurs at potentials greater than 0.7 V is due to oxidation of the melt.) The similarity of these cyclic voltammograms supports the contention that the addition of either WCl<sub>6</sub> or KWCl<sub>6</sub> to basic melt results in the same solute species. However, the rest potentials of working electrodes immersed in these solutions changed to more negative potentials after several hours, suggesting that the electroactive species introduced by addition of WCl<sub>6</sub> or KWCl<sub>6</sub> was undergoing slow conversion to yet another species.

Cyclic voltammetric data for the redox process with  $E_p^c = 0.42$  V are collected in Table I. These data were produced in a solution prepared from WCl<sub>6</sub>; however, identical results were obtained in a solution made with KWCl<sub>6</sub>. The voltammetric peak potential separation for these cyclic voltammograms averaged 0.067 V over the range of scan rates tested. (The theoretical value for a one-electron reversible charge transfer is 0.062 V at 40.0 °C). In addition, the peak current ratio,  $i_p^a/i_p^c$ , calculated by using Nicholson's procedure,<sup>27</sup> was close to 1 and the current function,  $i_p^c/\nu^{1/2}$ , was approximately constant over the same range of scan rates. The limiting current at a GCRDE varied linearly with the square root of rotation rate during reduction of a solution containing either WCl<sub>6</sub> or KWCl<sub>6</sub> (Figure 2). The information presented above indicates that this charge-transfer process is reversible and points to an absence of homogeneous chemical reactions coupled to the charge-transfer process.<sup>28</sup> The data collected

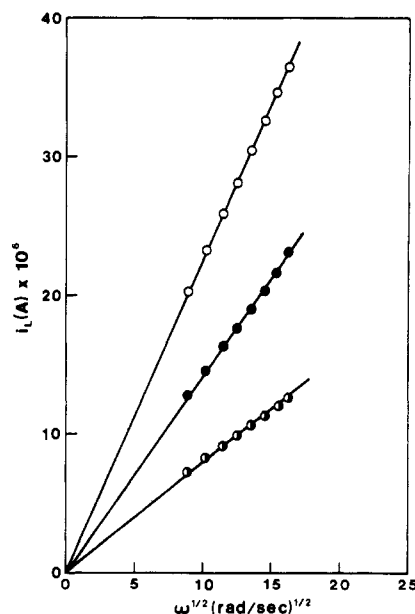


Figure 2. Plots of the limiting current at a GCRDE as a function of rotation rate in 44.4 mol % AlCl<sub>3</sub>-MEIC: (O) 9.3 × 10<sup>-3</sup> M in [WCl<sub>6</sub>]<sup>-</sup>,  $E_{app} = 0.25$  V; (●) 6.9 × 10<sup>-3</sup> M in [WCl<sub>6</sub>]<sup>2-</sup>,  $E_{app} = -0.98$  V; (●) 4.8 × 10<sup>-3</sup> M in [W<sub>2</sub>Cl<sub>9</sub>]<sup>3-</sup>,  $E_{app} = 0.10$  V.

in Table II suggest that this redox process is approximately independent of melt composition.

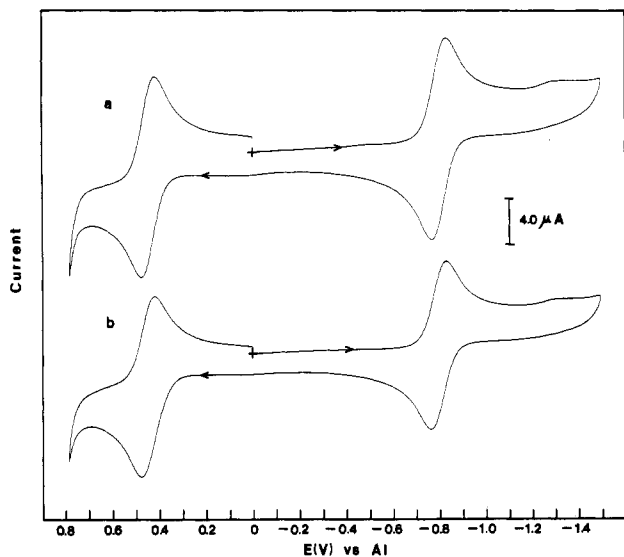
Controlled-potential coulometry was performed on fresh solutions of WCl<sub>6</sub> in basic melt. Exhaustive reduction at

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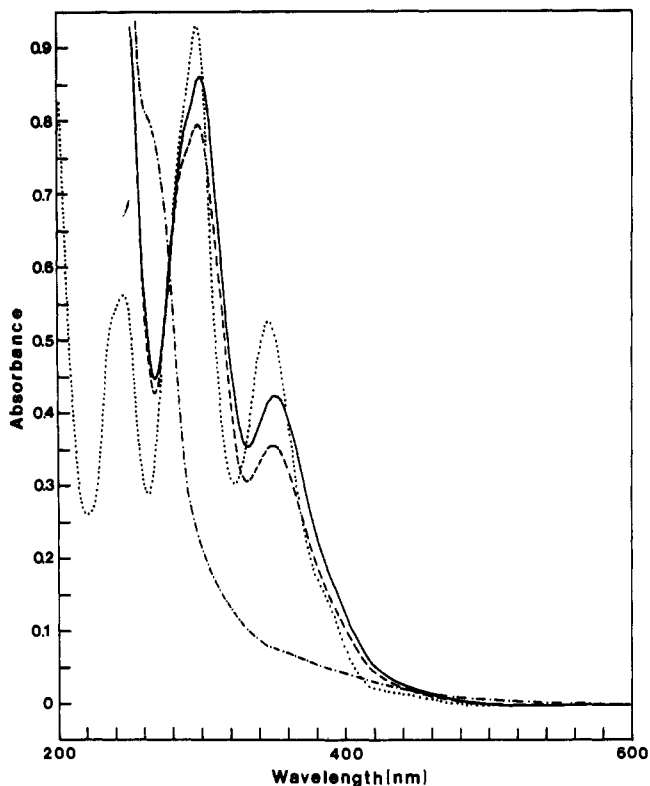
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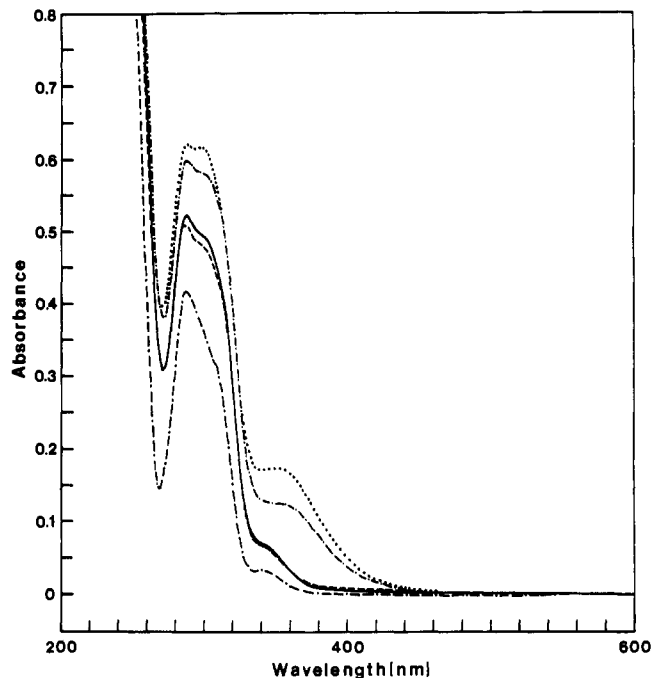
**Figure 3.** Cyclic voltammograms at a glassy-carbon electrode in 44.4 mol %  $\text{AlCl}_3$ -MEIC at 40.0 °C: (a) product obtained after exhaustive electrolytic reduction of a  $7.1 \times 10^{-3}$  M solution of  $\text{WCl}_6$  at  $E_{\text{appl}} = -0.30$  V; (b)  $6.1 \times 10^{-3}$  M in  $\text{K}_2\text{WCl}_6$ . Sweep rates were  $0.020 \text{ V s}^{-1}$ .



**Figure 4.** Tungsten(V) absorption spectra: (—)  $6.3 \times 10^{-5}$  M  $\text{WCl}_6$  in 44.4 mol % melt (vs. pure melt); (---)  $6.5 \times 10^{-5}$  M  $\text{KWCl}_6$  in 44.4 mol % melt (vs. pure melt); (····) pure 44.4 mol % melt (vs. air); (-·-·)  $7.5 \times 10^{-5}$  M  $\text{KWCl}_6$  in  $\text{CH}_3\text{CN}$  (vs. pure  $\text{CH}_3\text{CN}$ ).

potentials of  $-0.3$  and  $-0.5$  V gave  $n$  values of 1.0 and resulted in a pale green solution. A cyclic voltammogram of this solution initiated 10 mV negative of the working electrode rest potential (Figure 3a) indicates that the reduced form of the redox couple is present and that no significant amounts of other new electroactive species appear to be produced during electrolysis.

Absorption spectra of fresh solutions of  $\text{WCl}_6$  and  $\text{KWCl}_6$  in 44.4 mol % melt are shown in Figure 4. Data taken from these spectra are recorded in Table III. It can be seen readily



**Figure 5.** Tungsten(IV) absorption spectra: (—)  $6.6 \times 10^{-5}$  M in the product obtained after electrolytic reduction of a  $\text{WCl}_6$  solution in 44.4 mol % melt (vs. pure melt); (---)  $6.5 \times 10^{-5}$  M  $\text{K}_2\text{WCl}_6$  in 44.4 mol % melt (vs. pure melt); (-·-·)  $6.6 \times 10^{-5}$  M  $\text{KWCl}_6$  in 44.4 mol % melt after 72 h (vs. pure melt); (····)  $6.3 \times 10^{-5}$  M  $\text{WCl}_6$  in 44.4 mol % melt after 72 h; (-·-·)  $6.0 \times 10^{-5}$  M  $\text{K}_2\text{WCl}_6$  in  $\text{CH}_3\text{CN}$  (vs. pure  $\text{CH}_3\text{CN}$ ).

from this table and figure that the spectral characteristics of  $\text{WCl}_6$  and  $\text{KWCl}_6$  solutions are very similar and that they exhibit many features which are comparable to those observed for the  $[\text{WCl}_6]^-$  ion dissolved in organic solvents. It was not possible to record the spectrum of solutions made with basic melt below ca. 270 nm, since the UV cutoff of the melt occurs near this wavelength. Also, accurate values of the absorptivities for the maxima appearing in the  $\text{WCl}_6$  and  $\text{KWCl}_6$  spectra could not be calculated because the absorbancies associated with these maxima changed with time.

**$\text{K}_2\text{WCl}_6$ .** Solutions of  $\text{K}_2\text{WCl}_6$  in basic melt were pale green. It should be noted that dissolution of  $\text{K}_2\text{WCl}_6$  in liquid ammonia is reported to result in a solution of similar color.<sup>23</sup> A cyclic voltammogram of a solution of  $\text{K}_2\text{WCl}_6$  in 44.4 mol % melt is shown in Figure 3b. An absorption spectrum of a similar but more dilute solution of  $\text{K}_2\text{WCl}_6$  is depicted in Figure 5. Also shown in this figure is a spectrum of the solution resulting from the coulometric experiment described above.

Considered together, the evidence presented above suggests that the addition of  $\text{WCl}_6$  to basic melt results in the formation of the tungsten(V) chloro complex  $[\text{WCl}_6]^-$ . The first reduction process that appears in Figure 1 must therefore correspond to reversible redox reaction 1. Similar conversion



of tungsten(VI) to tungsten(V) was noted in molten  $\text{LiCl-KCl}$  at 450 °C and attributed to oxidation of chloride ion by tungsten(VI).<sup>16</sup> Acetonitrile also reduces tungsten(VI) to tungsten(V).<sup>19</sup> However,  $\text{WCl}_6$  is reported to be stable in molten  $\text{Al}_2\text{Cl}_6$  and both acidic and basic  $\text{AlCl}_3$ - $\text{NaCl}$  melt.<sup>31</sup> The reduction of  $\text{WCl}_6$  to  $[\text{WCl}_6]^-$  by  $\text{AlCl}_3$ -MEIC melt is probably due to oxidation of the organic component of the melt by the tungsten(V) species. The lack of a voltammetric re-

duction wave for dissolved chlorine either during or following the dissolution of  $WCl_6$  and the observed stability of  $WCl_6$  in a chloroaluminate melt with a cation that is much more resistant toward oxidation ( $AlCl_3-NaCl$ ) tend to support this premise.

Solutions of  $[WCl_6]^-$  in basic melt do not appear to exhibit long-term stability. The negative shift in the working electrode rest potential and the spectral similarity of aged solutions of  $WCl_6$  and  $KWCl_6$  to solutions prepared from  $K_2WCl_6$  (Figure 5) suggest that  $[WCl_6]^-$  is reduced to  $[WCl_6]^{2-}$  by a component of the melt after standing for long periods of time. Thus, the addition of  $WCl_6$  to basic  $AlCl_3$ -MEIC melt produces  $[WCl_6]^-$  immediately and eventually results in the formation of  $[WCl_6]^{2-}$ .

The  $[WCl_6]^{2-}$  anion can be reduced at  $-0.83$  V as shown in Figure 3. Cyclic voltammetric data for this reduction process are given in Table I. The GCRDE limiting current for reduction of  $[WCl_6]^{2-}$  is linear with the square root of rotation rate (Figure 2). A plot of  $\log [(i_L - i)/i]$  vs.  $E$ , constructed with GCRDE data, was linear and exhibited a slope of 65 mV in 44.4 mol % melt. The reduction of  $[WCl_6]^{2-}$  was approximately independent of melt composition over the range of melt compositions examined (Table II). It can be inferred from the GCRDE data and the data collected in Tables I and II that the reduction of  $[WCl_6]^{2-}$  takes place via a one-electron, reversible charge-transfer reaction, uncomplicated by coupled homogeneous reactions on the voltammetric time scale. Thus,  $[WCl_6]^{2-}$  is reduced to a monomeric tungsten(III) species,  $[WCl_6]^{3-}$ , as shown in eq 2.



These results are interesting in view of the fact that no monomeric tungsten(III) chloro complex containing  $[WCl_6]^{3-}$  appears to have been isolated.<sup>32</sup> However, a tungsten(III) monomer was suggested for dilute solutions of tungsten(III) in molten  $LiCl-KCl$  at 450 °C.<sup>17</sup> In addition, Hagedorn et al.<sup>19</sup> obtained a one-electron reduction for  $[WCl_6]^{2-}$  in  $CH_3CN$  and denoted the product to be  $[WCl_6]^{3-}$ .

Exhaustive controlled-potential electrolysis experiments were conducted at  $-1.10$  V in 44.4 and 40.2 mol % melts in an attempt to prepare stable solutions of  $[WCl_6]^{3-}$  by reduction of  $[WCl_6]^{2-}$ . A steady-state current was obtained a short time after the electrolysis experiment was commenced. Passage of charge in excess of 2.0 faradays/mol of  $[WCl_6]^{2-}$  resulted in the reduction of only small amounts of the tungsten(IV) complex and considerable darkening of the melt. These observations suggest that  $[WCl_6]^{2-}$  is probably regenerated by a slow coupled homogeneous reaction subsequent to its reduction during the time interval required for coulometry experiments.<sup>33</sup> The half-wave potential for the  $[WCl_6]^{2-}/[WCl_6]^{3-}$  couple ( $-0.80$  V) was found to be negative to that for the  $H^+/H_2$  couple in this melt ( $-0.44$  V). The basic  $AlCl_3$ -MEIC melt used in this study was found to contain hydrogen ion at a concentration comparable to that of the tungsten solutes. Thus, although the  $[WCl_6]^{2-}/[WCl_6]^{3-}$  electrode reaction appears uncomplicated on the voltammetric time interval, at longer times  $[WCl_6]^{3-}$  is oxidized to  $[WCl_6]^{2-}$  by the adventitious hydrogen ion. The heterogeneous kinetics for hydrogen ion reduction are very slow at glassy carbon in  $AlCl_3$ -MEIC melt. Hence, the presence of this species is not always obvious. The quasi-reversible reduction of hydrogen ion can be observed at pretreated platinum electrodes.<sup>34</sup>

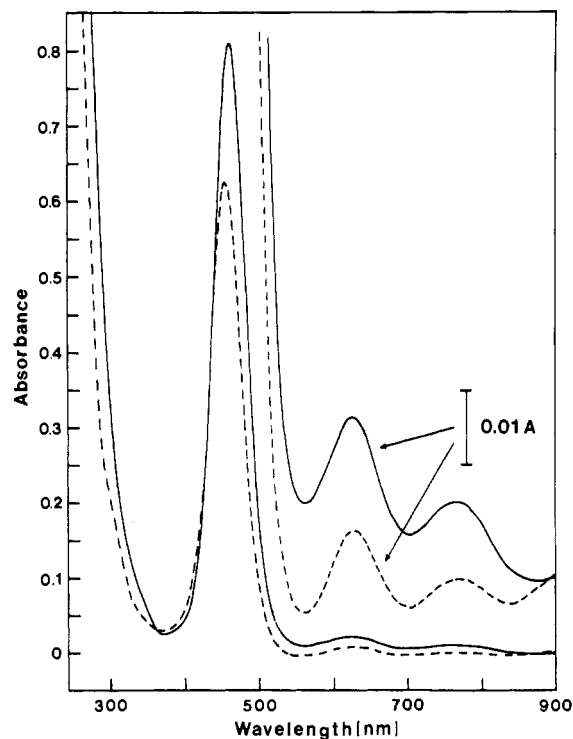


Figure 6. Tungsten(III) absorption spectra: (—)  $2.0 \times 10^{-4}$  M  $K_3W_2Cl_9$  in 44.4 mol %  $AlCl_3$ -MEIC melt (vs. pure melt); (---)  $1.7 \times 10^{-4}$  M  $K_3W_2Cl_9$  in 12 M HCl (vs. pure 12 M HCl).

It should be noted that the introduction of very small amounts of hydrogen ion into the melt appears unavoidable at the present time. Methods available for removing hydrogen ion, e.g., coulometric reduction at platinum or addition of active metals, were unsatisfactory. In the former case large-area platinum electrodes were poisoned rapidly during reduction. Active metals like lithium or sodium appear to decompose the melt. Thus, the practical negative limit of basic  $AlCl_3$ -MEIC is about  $-0.40$  V.

$K_3W_2Cl_9$ . The addition of  $K_3W_2Cl_9$  to 44.4 mol %  $AlCl_3$ -MEIC melt produced a dark yellow-green or olive-colored solution. An absorption spectrum of this solution (Figure 6 and Table III) is very similar to that observed for  $K_3W_2Cl_9$  in 12 M HCl, confirming the presence of the metal-bonded cluster ion  $[W_2Cl_9]^{3-}$ . This species appears to be quite stable in this melt but is reported to disproportionate in  $LiCl-KCl$  eutectic at 450 °C.<sup>16</sup>

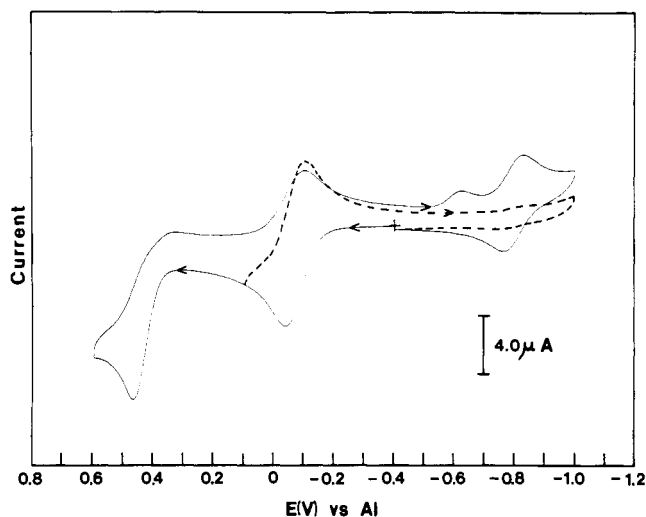
The electrochemical behavior of this species on a time scale corresponding to voltammetry was considerably different from the behavior observed on the longer time interval required for bulk controlled-potential electrolysis experiments. Cyclic voltammograms initiated approximately 0.15 V negative of the solution rest potential are shown in Figure 7. If the working electrode is scanned in the positive direction, two oxidation waves with peak potentials of ca.  $-0.04$  and  $0.46$  V are observed. The first oxidation wave has an associated reduction wave at  $-0.10$  V, but the second oxidation wave, although approximately equal in height to the first wave, does not exhibit a significant reverse current.

Cyclic voltammetric data for the first oxidation wave are recorded in Table I. These data suggest a one-electron, reversible charge-transfer process uncomplicated by coupled homogeneous chemical reactions. A plot of the GCRDE limiting current for this wave is linear with the square root of rotation rate (Figure 2). A plot of  $\log [(i_L - i)/i]$  vs.  $E$  for a GCRDE wave at a rotation rate of  $157 \text{ rad s}^{-1}$  was linear,

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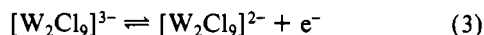
(33) Meites, L. "Physical Methods of Chemistry, Part IIA: Electrochemical Methods"; Weissberger, A., Rossiter, B. W., Eds.; Wiley: New York, 1971; Vol. I, Chapter 9.

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**Figure 7.** Cyclic voltammograms at a glassy-carbon electrode of a  $3.23 \times 10^{-3}$  M solution of  $K_3W_2Cl_9$  in 44.4 mol %  $AlCl_3$ -MEIC melt at 40.0 °C: (—) scan reversed at 0.6 V; (---) scan reversed at 0.1 V. Sweep rates were  $50 \text{ mV s}^{-1}$ .

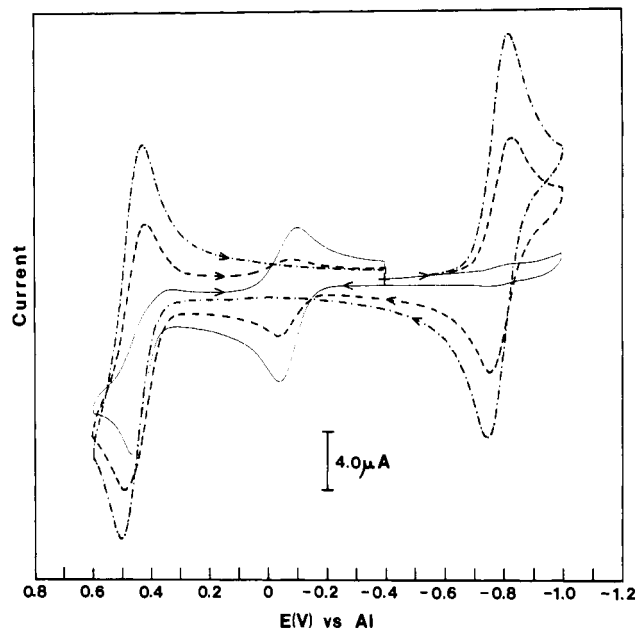
exhibited a slope of 62 mV, and gave an intercept ( $E_{1/2}$ ) of  $-0.076$  V. The last value was in good agreement with an estimate of  $E_{1/2} = -0.080$  V, determined with use of cyclic voltammetry. Voltammetric data for the first oxidation wave were approximately independent of melt composition (Table II). Therefore, this wave must correspond to the formation of a dimeric mixed-valence tungsten species,  $[W_2Cl_9]^{2-}$ , via reaction 3. The formal oxidation state of tungsten in this



complex is +3.5. It is interesting to note that Saillant and Wentworth<sup>35</sup> have reported the isolation of a complex containing  $[W_2Cl_9]^{2-}$  produced by chemical oxidation of  $[W_2Cl_9]^{3-}$ .

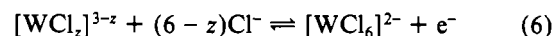
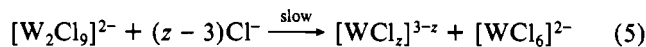
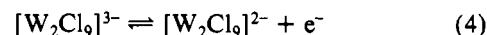
The stability of the  $[W_2Cl_9]^{2-}$  species produced by the one-electron oxidation of  $[W_2Cl_9]^{3-}$  was examined in 44.4 and 41.2 mol % melt with use of controlled-potential coulometry. Exhaustive electrolysis was performed at an applied potential of 0.15 V and gave  $n$  values of 2.0 in both melts. Cyclic voltammograms of the 44.4 mol % melt, recorded after the passage of 0, 100%, and 180% of the charge necessary for one-electron oxidation of the total amount of  $[W_2Cl_9]^{3-}$ , are shown in Figure 8. After the passage of 100% of the charge for  $n = 1$  or 1.0 faraday/mol of  $[W_2Cl_9]^{3-}$ , the height of the  $[W_2Cl_9]^{3-}$  oxidation wave at  $-0.04$  V has decreased by half relative to that found in the original solution. In addition, a reduction wave for  $[WCl_6]^{2-}$  at  $-0.83$  V is present. If appropriate adjustments are made for the differences in the  $[W_2Cl_9]^{3-}$  and  $[WCl_6]^{2-}$  diffusion coefficients (vide infra), it can be shown that the height of the  $[WCl_6]^{2-}$  reduction wave in this solution corresponds to a concentration of  $[WCl_6]^{2-}$  that is twice that of the unoxidized  $[W_2Cl_9]^{3-}$ . A cyclic voltammogram recorded after the passage of 1.8 faradays/mol of  $[W_2Cl_9]^{3-}$  is very similar to that obtained for a solution in which  $[WCl_6]^{2-}$  is the major electroactive solute (Figure 3). The height of the  $[WCl_6]^{2-}$  reduction wave, adjusted as described above, indicates that 90% of the original  $[W_2Cl_9]^{3-}$  has been oxidized to  $[WCl_6]^{2-}$ . The electrolysis current decayed to a very small value after 2.0 faradays/mol of  $[W_2Cl_9]^{3-}$  were accumulated.

Thus,  $[W_2Cl_9]^{3-}$  exhibits a one-electron oxidation to  $[W_2Cl_9]^{2-}$  on the voltammetric time interval but undergoes a two-electron oxidation to  $[WCl_6]^{2-}$  during the time required



**Figure 8.** Cyclic voltammograms at a glassy-carbon electrode in 44.4 mol %  $AlCl_3$ -MEIC melt at 40.0 °C: (—)  $3.23 \times 10^{-3}$  M in  $K_3W_2Cl_9$ ; (---) same solution after the passage of 1.0 faraday/mol of  $K_3W_2Cl_9$  at  $E_{\text{appl}} = 0.10$  V; (-.-.-) same solution after the passage of 1.8 faraday/mol of  $K_3W_2Cl_9$ .

to carry out exhaustive controlled-potential electrolysis. A reasonable ECE mechanism which leads to the formation of  $[WCl_6]^{2-}$  through slow disproportionation of  $[W_2Cl_9]^{2-}$  to  $[WCl_6]^{2-}$  and a monomeric tungsten(III) species can be proposed on the basis of the experimental data (eq 4-6). The



monomeric tungsten(III) species, produced in the disproportionation step,  $[WCl_z]^{3-z}$ , is further oxidized to  $[WCl_6]^{2-}$  at the electrolysis potential as represented in eq 6. These results suggest that exhaustive electrolysis experiments performed at applied potentials greater than ca. 0.5 V should consume 4.0 faradays/mol of  $[W_2Cl_9]^{3-}$  and produce a solution containing only  $[WCl_6]^{2-}$ , if the latter species were completely stable in solution. Coulometric oxidation of a  $[W_2Cl_9]^{3-}$  solution in 44.4 mol % melt at this applied potential did in fact require approximately 4 faradays/mol of complex. A cyclic voltammogram of the resulting solution was very similar to those for solutions of  $[WCl_6]^{2-}$  (Figure 1), confirming the expected result.

The second voltammetric oxidation wave observed in  $[W_2Cl_9]^{3-}$  solutions (Figure 7) is approximately equal in height to the first wave at scan rates of  $50 \text{ mV s}^{-1}$  or more. Interestingly, no reverse current was detected for this wave at the fastest scan rate tested,  $10 \text{ V s}^{-1}$ , indicating rapid decomposition of the species produced by one-electron oxidation of  $[W_2Cl_9]^{2-}$ . The height of the second oxidation wave increases relative to that of the first wave as the voltammetric scan rate is decreased below  $50 \text{ mV s}^{-1}$ , and it is about 1.6 times the height of the first wave at  $10 \text{ mV s}^{-1}$ . In addition, a small reverse current can be observed following the second oxidation wave at this scan rate. These observations suggest that the oxidation of  $[W_2Cl_9]^{2-}$  consumes more than one electron per  $[W_2Cl_9]^{2-}$  ion at slow scan rates, and they point to an ECE or similar mechanism for oxidation of  $[W_2Cl_9]^{2-}$  under these conditions. The identity of the products resulting from the voltammetric oxidation of  $[W_2Cl_9]^{2-}$  could not be determined with certainty, but the reduction waves at  $-0.63$  and  $-0.83$  V

**Table IV.** Voltammetric Data for Ferrocene at Different Melt Compositions

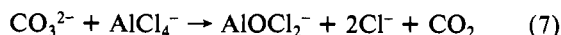
mol % AlCl <sub>3</sub>	pCl	$E_p^a$ , V	$E_{1/2}^a$ , V	$10^6 \eta D_1^b$ , g cm s <sup>-2</sup>
49.5	1.043	0.250	0.217	11.9
48.9	0.719	0.254	0.223	12.0
48.2	0.508	0.257	0.224	11.9
47.7	0.401	0.257	0.224	11.4
47.2	0.318	0.258	0.226	11.7
45.1	0.099	0.261	0.229	11.3
43.2	-0.026	0.264	0.231	11.5
av				11.7 ± 0.3

<sup>a</sup> Estimated from  $(E_p^a + E_p^c)/2$  at a scan rate of 50 mV s<sup>-1</sup>.

<sup>b</sup> Calculated from GCRDE data.

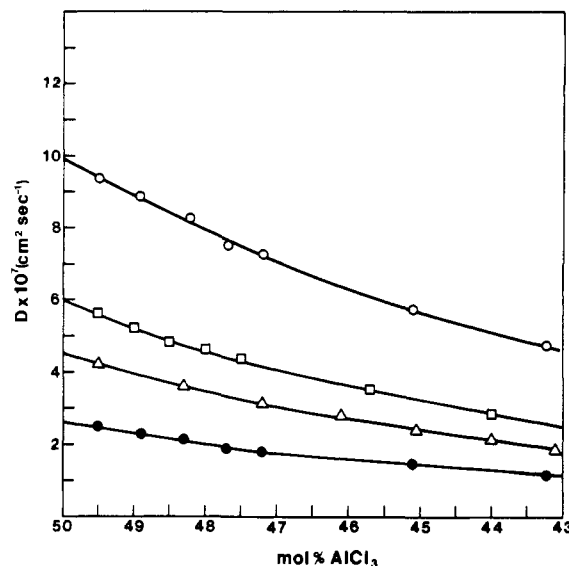
(Figure 7) suggest that substantial amounts of  $[\text{WCl}_6]^{2-}$  and another unidentified species are present in the electrode diffusion layer after the second oxidation wave is traversed.

**Addition of Oxide to  $[\text{WCl}_6]^-$ ,  $[\text{WCl}_6]^{2-}$ , and  $[\text{W}_2\text{Cl}_9]^{3-}$  Solutions.** The addition of  $\text{Li}_2\text{CO}_3$  to basic chloroaluminate melts has been shown to result in the formation of  $\text{AlOCl}_2^-$  according to reaction 7.<sup>36,37</sup> Both  $[\text{TiCl}_6]^{2-}$  and  $[\text{MoCl}_6]^{2-}$  appear to



react with  $\text{AlOCl}_2^-$  to form oxychloro complexes.<sup>10,11</sup>  $\text{Li}_2\text{CO}_3$  was added to basic melt containing  $[\text{WCl}_6]^-$ ,  $[\text{WCl}_6]^{2-}$ , or  $[\text{W}_2\text{Cl}_9]^{3-}$ . However, the formation of the corresponding oxychloro complexes via interaction of  $\text{AlOCl}_2^-$  with these species does not seem to be favored in this case, since no outward change in the voltammetric properties of these solutions could be detected; i.e., no new peaks were observed and no changes in the heights of existing peaks were noted after several hours elapsed. These results are especially surprising in the case of tungsten(V), since numerous oxychlorides and oxychloro complexes are known.<sup>32</sup> Apparently, reactions of  $\text{AlOCl}_2^-$  with  $[\text{WCl}_6]^-$  in basic  $\text{AlCl}_3$ -MEIC are not thermodynamically favorable or they occur very slowly.

**Diffusion Coefficients.** Diffusion coefficients for  $[\text{WCl}_6]^-$ ,  $[\text{WCl}_6]^{2-}$ , and  $[\text{W}_2\text{Cl}_9]^{3-}$  were calculated as a function of melt composition from GCRDE limiting current data and the viscosity data of Wilkes et al.<sup>38</sup> Figure 9 shows a plot of these diffusion coefficients as a function of melt composition. Data for ferrocene are included for comparison. The approximate constancy of the Stokes-Einstein product,  $\eta D$ , for the tungsten chloro complexes and ferrocene (Tables II and IV) indicates that the large changes in the diffusion coefficients shown in this figure arise principally from changes in the viscosity of the melt. However,  $\eta D$  for all of the tungsten chloro complexes exhibits a small decrease as the melt is made more basic, while this product is essentially constant for ferrocene. This implies that the average solvodynamic radius of each tungsten species increases slightly with increasing basicity. In the absence of solvation (vide infra) this leads one to suspect the presence of more than one tungsten chloro complex for each oxidation state, although the voltammetric and spectral data indicate that  $[\text{WCl}_6]^-$ ,  $[\text{WCl}_6]^{2-}$ , and  $[\text{W}_2\text{Cl}_9]^{3-}$  are decidedly the dominant species. The formation of complexes containing fewer chlorides with radii smaller than the prevalent complexes



**Figure 9.** Variation of the diffusion coefficients for ferrocene and tungsten chloro complexes in basic  $\text{AlCl}_3$ -MEIC melt at 40.0 °C: (O) ferrocene; (□)  $[\text{WCl}_6]^-$ ; (Δ)  $[\text{WCl}_6]^{2-}$ ; (●)  $[\text{W}_2\text{Cl}_9]^{3-}$ .

would be most likely close to the 50 mol % composition in accord with the trend in  $\eta D$  values that is observed in Table II.

The average diffusion coefficients obtained for  $[\text{WCl}_6]^-$ ,  $[\text{WCl}_6]^{2-}$ , and  $[\text{W}_2\text{Cl}_9]^{3-}$  from several individual determinations in 44.4 mol % melt are  $(2.8 \pm 0.2) \times 10^{-7}$ ,  $(2.2 \pm 0.1) \times 10^{-7}$ , and  $(1.5 \pm 0.1) \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>, respectively. Solvodynamic radii of 3.8 and 4.8 Å were calculated for  $[\text{WCl}_6]^-$  and  $[\text{WCl}_6]^{2-}$ , respectively, by using the Stokes-Einstein equation (eq 8). An estimate of the structural radius for

$$\frac{kT}{D\pi\eta} = 6 \quad (8)$$

$[\text{WCl}_6]^{2-}$ , calculated from the crystal radii of  $\text{W}^{4+}$  and  $\text{Cl}^-$ , assuming that the complexes were spherical, was about 4.3 Å. The structural radius of  $[\text{WCl}_6]^-$ , which contains  $\text{W}^{5+}$ , should be slightly smaller as a result of the greater positive charge on  $\text{W}^{5+}$ . The good agreement between the calculated solvodynamic and structural radii observed for both  $[\text{WCl}_6]^-$  and  $[\text{WCl}_6]^{2-}$  in 44.4 mol % melt and the approximate constancy of  $\eta D$  for these species (Table II) suggest that these anions are probably unsolvated in basic melt. It should be pointed out that the good agreement observed between the structural radii and solvodynamic radii found in this and other studies conducted in chloroaluminate melts may be fortuitous. McLaughlin<sup>39</sup> has proposed a modification to eq 8 for systems in which the radius of the diffusing species is identical with that of the solvent. This modification involves replacing the value of 6 in eq 8 with 4. If applied to the data presented here, it would lead to solvodynamic radii that are 50% larger.

**Acknowledgment.** This work was supported by the National Science Foundation through Grant No. CHE-8025235.

**Registry No.** MEIC, 65039-09-0;  $\text{WCl}_6$ , 13283-01-7;  $\text{KWCl}_6$ , 17156-79-5;  $\text{K}_2\text{WCl}_6$ , 16923-43-6;  $\text{K}_3\text{W}_2\text{Cl}_9$ , 23403-17-0;  $[\text{WCl}_6]^-$ , 44493-03-0;  $[\text{WCl}_6]^{2-}$ , 20581-18-4;  $[\text{WCl}_6]^{3-}$ , 30617-02-8;  $[\text{W}_2\text{Cl}_9]^{3-}$ , 26443-76-5;  $[\text{WCl}_9]^{2-}$ , 39448-64-1;  $\text{AlCl}_3$ , 7446-70-0; W, 7440-33-7; ferrocene, 102-54-5.

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