

Contribution from the Institute of Mineral Industry and Molten Salts Group, Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark, and Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996-1600

## Electrochemical and Spectroscopic Studies of Tantalum Species in NaCl-AlCl<sub>3</sub> Melts at 160-300 °C

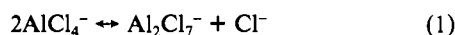
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The formation of complexes of Ta(V) in NaCl-AlCl<sub>3</sub> melts at 175 and 300 °C has been studied by potentiometric and spectrophotometric methods. The results at 175 °C could, within the pCl range 1.13-ca. 4.5 and with the Ta(V) concentration in the range 0-0.3 M, best be explained by the equilibrium  $\text{TaCl}_6^- \leftrightarrow \text{TaCl}_5 + \text{Cl}^-$  with a pK value (based on molar concentration) of 3.89 (4) and a solubility limit for TaCl<sub>5</sub> of 0.087 (9) M. However, equilibria involving Ta<sub>2</sub>Cl<sub>10</sub> could not be ruled out. UV-visible spectra of pure TaCl<sub>5</sub> and TaCl<sub>6</sub><sup>-</sup> were very difficult to obtain because of the formation of oxo chloro species. The electrochemical reduction of Ta(V) in AlCl<sub>3</sub>-rich melts results in the formation of Ta(IV) followed by dimerization and further reduction to Ta<sub>6</sub>Cl<sub>14</sub> and possibly other tantalum clusters. Formation of metallic tantalum was not observed in the electrolysis.

### Introduction

Molten chloroaluminates have considerable interest, partly because of their ability to stabilize lower oxidation states of a number of elements, such as Hg, Cd, Bi, S, Se, and Te, and partly because of their uses in applications such as batteries. A review of chemistry in molten chloroaluminates is available.<sup>1</sup> The coordination and redox chemistry in these melts is a sensitive function of the chloro acidity (pCl) and the temperature. The acid-base properties in AlCl<sub>3</sub>-NaCl melts near the 50-50 mol % composition can be described by the equilibrium<sup>2-4</sup>



In more acidic melts (i.e. melts with higher AlCl<sub>3</sub> content) other species such as Al<sub>3</sub>Cl<sub>10</sub><sup>-</sup> and Al<sub>2</sub>Cl<sub>6</sub>, have to be taken into consideration to explain Raman spectroscopic,<sup>5</sup> potentiometric,<sup>2,3</sup> and vapor pressure<sup>2</sup> measurements on these melts.

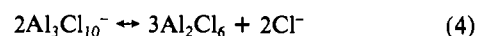
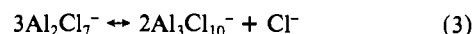
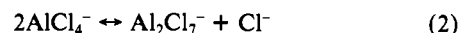
As part of our general studies of chloroaluminate melts, the present paper describes an investigation of the complex formation and redox chemistry of tantalum(V) in NaCl-AlCl<sub>3</sub> melts.

Molten TaCl<sub>5</sub> consists of molecular Ta<sub>2</sub>Cl<sub>10</sub> at 220 °C, which gradually dissociates to TaCl<sub>5</sub> as the temperature is raised.<sup>6</sup> TaCl<sub>5</sub> molecules of D<sub>3h</sub> symmetry are also known to exist in the vapor phase.<sup>7</sup> An examination of the binary NaCl-TaCl<sub>5</sub> system<sup>8</sup> shows the presence of the compound NaTaCl<sub>6</sub>, which melts incongruently at 470 °C. The fact that TaCl<sub>5</sub> is a Lewis acid having a strong affinity for chloride ions is also seen from the formation of octahedral TaCl<sub>6</sub><sup>-</sup> ions in the equimolar KCl-TaCl<sub>5</sub><sup>6</sup> and NaCl-TaCl<sub>5</sub><sup>9</sup> melts and in basic and neutral solutions of TaCl<sub>5</sub> in NaCl-AlCl<sub>3</sub> melts<sup>6</sup> as well as in basic MeEtimCl-AlCl<sub>3</sub> solutions (MeEtim = 1-methyl-3-ethylimidazolium).<sup>10</sup> For acidic solutions of TaCl<sub>5</sub> in NaCl-AlCl<sub>3</sub> melts, Raman spectra indicate that molecular TaCl<sub>5</sub> is present at temperatures above 250 °C whereas Ta<sub>2</sub>Cl<sub>10</sub> is the major species formed at lower temperatures.<sup>6</sup> This behavior is similar to that of NbCl<sub>5</sub> dissolved in KCl-AlCl<sub>3</sub><sup>11,12</sup> and in NaCl-AlCl<sub>3</sub> melts,<sup>12</sup> where NbCl<sub>6</sub><sup>-</sup> is formed in basic solutions and NbCl<sub>5</sub> is found at high temperatures in acidic solutions whereas low temperatures stabilize Nb<sub>2</sub>Cl<sub>10</sub>.

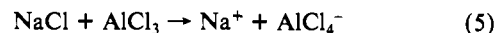
### General Considerations

In the present work, the formal concentration C' of one of the added substances is defined as the initial molar amount dissolved in 1 L of the melt (unit: F). Real molar concentrations are symbolized by brackets. The volumes of the melts are calculated by assuming ideal mixing of NaCl-AlCl<sub>3</sub> and TaCl<sub>5</sub>. This assumption results only in minor errors since the amounts of TaCl<sub>5</sub> are small compared to the amounts of AlCl<sub>3</sub> and NaCl. The densities of AlCl<sub>3</sub>-NaCl and of TaCl<sub>5</sub> were obtained from the work of Berg et al.<sup>13</sup> and of Nisel'son et al.,<sup>14</sup> respectively. pCl is defined as the negative logarithm of the chloride ion molarity. Three

equilibria were used to describe the behavior of the NaCl-AlCl<sub>3</sub> molten system:



The pK values (in molar units) for reactions 2-4 used in the calculations are 7.05, 6.9, and 14 at 175 °C,<sup>2</sup> respectively. Since AlCl<sub>3</sub> contained small amounts of AlOCl, it was necessary to correct the melt composition. The AlOCl contents can be calculated from potentiometric measurements on the equimolar NaCl-AlCl<sub>3</sub> solvent. NaCl and AlCl<sub>3</sub> react almost quantitatively as follows:



However, in most cases an excess of NaCl relative to AlCl<sub>3</sub> that cannot be explained by a weighing error is observed. This is due to the presence of AlOCl in AlCl<sub>3</sub>, since AlOCl does not react with NaCl in the pCl range investigated.<sup>15</sup>

AlOCl will further react with TaCl<sub>5</sub> in the melt<sup>16</sup> according to



From potentiometric measurements on 0.3 F solutions of TaOCl<sub>3</sub> dissolved in NaCl-AlCl<sub>3</sub> melts performed at Lyngby,<sup>16</sup> we know

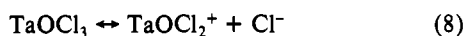
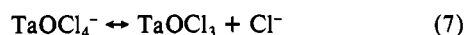
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that TaOCl<sub>3</sub> takes part in the equilibria:



with the p*K* values 2.74 (p*K*<sub>7</sub>) and 4.52 (p*K*<sub>8</sub>).

Taking into consideration the above information, the experimental average coordination number of Ta(V) (in relation to pure chloride species) becomes

$$\bar{n}_{\text{Ta(V)}} = (C'_{\text{NaCl}} + 3C'_{\text{AlCl}_3} + 5C'_{\text{TaCl}_5} + C'_{\text{AlOCl}} - 4[\text{AlCl}_4^-] - 7[\text{Al}_2\text{Cl}_7^-] - 10[\text{Al}_3\text{Cl}_{10}^-] - 6[\text{Al}_2\text{Cl}_6] - 4[\text{TaOCl}_4^-] - 3[\text{TaOCl}_3] - 2[\text{TaOCl}_2^+] - [\text{Cl}^-]) / (C'_{\text{TaCl}_5} - C'_{\text{AlOCl}}) \quad (9)$$

In the present case where we are dealing with solute species with a limited solubility, it is, however, important to define a number that can be used when a precipitate is present and in this way utilize a larger compositional range. Such a number<sup>17</sup> can be expressed by  $\bar{n}'$ , which in the present case is defined in eq 10, where

$$\bar{n}'_{\text{Ta(V)}} = (C'_{\text{NaCl}} + 3C'_{\text{AlCl}_3} + 5n_{\text{TaCl}_5, \text{w}}/V + C'_{\text{AlOCl}} - 4[\text{AlCl}_4^-] - 7[\text{Al}_2\text{Cl}_7^-] - 10[\text{Al}_3\text{Cl}_{10}^-] - 6[\text{Al}_2\text{Cl}_6] - 4[\text{TaOCl}_4^-] - 3[\text{TaOCl}_3] - 2[\text{TaOCl}_2^+] - [\text{Cl}^-])V / (n_{\text{TaCl}_5, \text{w}} - n_{\text{AlOCl, w}}) \quad (10)$$

$n_{\text{TaCl}_5, \text{w}}$  is the total number of moles of TaCl<sub>5</sub> that was weighed (but not necessarily the number of moles in solution). (In this way we obtain an average coordination number including both precipitate and solution.)  $n_{\text{AlOCl, w}}$  is a similar number for the AlOCl impurity in the AlCl<sub>3</sub> used. This impurity amounts to about 0.2 mol % of the used AlCl<sub>3</sub> or 0.016 F in a melt (without Ta(V)). This value has been determined potentiometrically as described earlier.<sup>18</sup> *V* is the volume of the melt.

The electrochemical cell used for the potentiometric measurements was a chlorine–chlorine concentration cell:<sup>19</sup>

glassy carbon, Cl<sub>2</sub>||[Cl<sup>-</sup>]<sub>I</sub> (NaCl–AlCl<sub>3</sub>–TaCl<sub>5</sub>)  
|ceramic pin|[Cl<sup>-</sup>]<sub>II</sub> (NaCl<sub>sat</sub>–AlCl<sub>3</sub>)|Cl<sub>2</sub>, glassy carbon

I and II refer to measuring and reference compartments, respectively. It has been shown previously<sup>20,21</sup> that, in KCl–AlCl<sub>3</sub> melts near the 1:1 composition, cell potential, within experimental uncertainties, is given by

$$E = \frac{-RT}{F} \ln \frac{[\text{Cl}^-]_{\text{II}}}{[\text{Cl}^-]_{\text{I}}} \quad (11)$$

Similar calculations on the NaCl–AlCl<sub>3</sub> system<sup>2</sup> show that eq 11 is valid also in the compositional range 0.51 >  $X_{\text{NaCl}}$  > 0.49 investigated in this work. The pCl of the melt in the measuring compartment can then be expressed as

$$\text{pCl}_I = -(F/(RT \ln 10))\Delta E + \text{pCl}_{\text{II}} \quad (12)$$

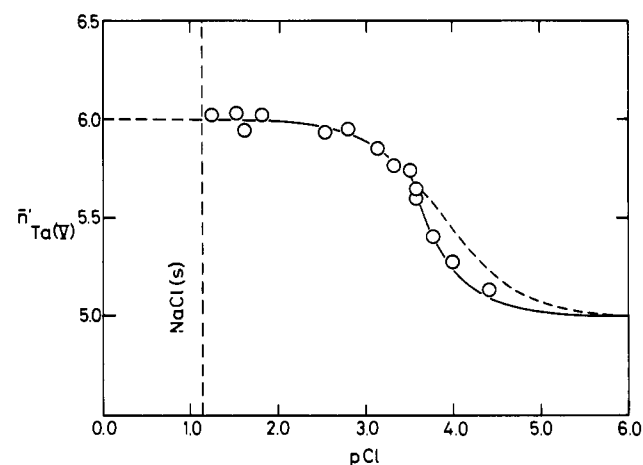
where pCl<sub>II</sub> is the pCl of a NaAlCl<sub>4</sub> melt saturated with NaCl used as the reference electrode. The pCl<sub>II</sub> value is 1.128 at 175 °C.<sup>2,3</sup>

In the spectrophotometric work, the Bouguer–Beer law and the law of additive absorbances were assumed to be valid. The formal absorptivity of TaCl<sub>5</sub> is the absorbance divided by the product of the path length and the formality of TaCl<sub>5</sub>. The absorbances for the liquid-phase spectra were corrected for the absorbance of the solvent and the amount of the Ta(V) oxo chloro species present in the melt as well as the TaCl<sub>5</sub> in gas phase above the melt (see later).

**Table I.** Cell Potentials and Compositions of 0.23–0.30 F Solutions of TaCl<sub>5</sub> in Molten NaCl–AlCl<sub>3</sub> at 175 °C

–Δ <i>E</i> , V	mole fractions <sup>a</sup>		
	NaCl	AlCl <sub>3</sub>	TaCl <sub>5</sub>
292.0 <sup>b</sup>	0.4878 <sub>0</sub>	0.4950 <sub>5</sub>	0.0171 <sub>5</sub>
254.8 <sup>b</sup>	0.4919 <sub>2</sub>	0.4907 <sub>8</sub>	0.0173 <sub>0</sub>
235.39 <sup>b</sup>	0.4933 <sub>8</sub>	0.4891 <sub>4</sub>	0.0161 <sub>6</sub>
217.82	0.4950 <sub>4</sub>	0.4879 <sub>3</sub>	0.0129 <sub>8</sub>
217.56 <sup>b</sup>	0.4957 <sub>3</sub>	0.4873 <sub>0</sub>	0.0163 <sub>5</sub>
212.21	0.4966 <sub>6</sub>	0.4863 <sub>5</sub>	0.0154 <sub>1</sub>
195.90	0.4963 <sub>5</sub>	0.4865 <sub>8</sub>	0.0130 <sub>1</sub>
179.20	0.4980 <sub>7</sub>	0.4846 <sub>1</sub>	0.0160 <sub>1</sub>
148.94	0.4991 <sub>0</sub>	0.4838 <sub>2</sub>	0.0154 <sub>9</sub>
125.42	0.4992 <sub>2</sub>	0.4835 <sub>0</sub>	0.0159 <sub>8</sub>
61.62	0.5005 <sub>5</sub>	0.4822 <sub>7</sub>	0.0165 <sub>6</sub>
43.54	0.5001 <sub>7</sub>	0.4825 <sub>9</sub>	0.0159 <sub>5</sub>
35.45	0.5011 <sub>1</sub>	0.4822 <sub>3</sub>	0.0166 <sub>6</sub>
10.40	0.5017 <sub>9</sub>	0.4815 <sub>3</sub>	0.0166 <sub>8</sub>

<sup>a</sup> Corrected for the presence of AlOCl in the solvent, assuming quantitative reaction between AlOCl and TaCl<sub>5</sub> producing AlCl<sub>3</sub> and TaOCl<sub>3</sub>. <sup>b</sup> Precipitate present (visual inspection).



**Figure 1.** Average experimental coordination number (with precipitate included) ( $\bar{n}_{\text{Ta(V)}}$ ) for Ta(V) in NaCl–AlCl<sub>3</sub> at 175 °C as a function of pCl. The formal concentrations (in the pCl range where no precipitate was present) were 0.23–0.30 F. Calculated values of  $\bar{n}'$  (for the reaction TaCl<sub>6</sub><sup>-</sup> ↔ TaCl<sub>5</sub> + Cl<sup>-</sup>) are indicated by a full curve. The dashed curve shows for a hypothetical extrapolation what would happen if no precipitation occurred. The vertical dashed line shows the limiting pCl, due to saturation with NaCl.

## Experimental Section

AlCl<sub>3</sub> and NaCl were prepared as described previously.<sup>2,21</sup> The solvent melts were formed by weighing the proper amounts of AlCl<sub>3</sub> and NaCl in nitrogen-filled dryboxes with measured water contents of approximately 5 ppm or less.

TaCl<sub>5</sub> (99.9% from Fluka) was purified by sublimation at 200 °C. Two different batches of TaCl<sub>5</sub> were made for the spectrophotometric measurements. The first had a chlorine content of 49.21 ± 0.21%, and the second, a content of 47.46 ± 0.23%. Both values were obtained as an average of four measurements and should be compared with the theoretical value of 49.49%. Thus, it can be seen that the first batch consists of almost pure TaCl<sub>5</sub> whereas the second batch must contain a certain amount of oxide chloride. In the experiments where the latter batch was used, a correction was made for the oxide chloride content (see below).

The chlorine/chloride electrode cell<sup>19</sup> used for the potentiometric measurements, as well as the furnace used, has been described previously.<sup>22,23</sup> The connecting tube between the two compartments of this cell was sealed after the addition of TaCl<sub>5</sub> in order to prevent distillation from one chamber to the other. The optical cells used for the spectrophotometric measurements were of fused quartz (Ultrasil from Hellma). Due to the large molar absorptivity of Ta(V), it was necessary to use cells

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**Table II.**  $pK$  Values, Solubilities, and Variances for Different Models of Chloro Complex Formation of Ta(V) in NaCl–AlCl<sub>3</sub> Melts at 175 °C<sup>a</sup>

equilibria	$pK_1$	$pK_2$	solubility [TaCl <sub>5</sub> ] <sub>max</sub> , M	var × 10 <sup>4</sup>
TaCl <sub>6</sub> <sup>-</sup> ↔ TaCl <sub>5</sub> + Cl <sup>-</sup>	3.89 (4)		0.087 (9)	10.8*
TaCl <sub>5</sub> ↔ TaCl <sub>5</sub> (s)				
2TaCl <sub>6</sub> <sup>-</sup> ↔ Ta <sub>2</sub> Cl <sub>10</sub> + 2Cl <sup>-</sup>	7.27 (8)		0.03 (3)	100.0
Ta <sub>2</sub> Cl <sub>10</sub> ↔ 2TaCl <sub>5</sub> (s)				
TaCl <sub>6</sub> <sup>-</sup> ↔ TaCl <sub>5</sub> + Cl <sup>-</sup>	3.95 (6)	-0.33 (19)	0.019 (7)	24.0*
2TaCl <sub>5</sub> ↔ Ta <sub>2</sub> Cl <sub>10</sub>				
Ta <sub>2</sub> Cl <sub>10</sub> ↔ 2TaCl <sub>5</sub> (s)				
TaCl <sub>6</sub> <sup>-</sup> ↔ TaCl <sub>5</sub> + Cl <sup>-</sup>	3.91 (13)	0.5 (31)	0.08 (3)	12.6*
2TaCl <sub>5</sub> ↔ Ta <sub>2</sub> Cl <sub>10</sub>				
TaCl <sub>5</sub> ↔ TaCl <sub>5</sub> (s)				

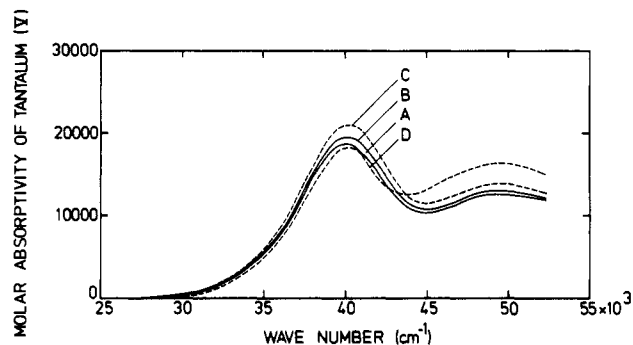
<sup>a</sup> Number of measurements 10 (number of different cells 5). Asterisks: based on  $F_{0.10}(9.3) = 5.24$  and  $F_{0.10}(8.3) = 5.25$ .

with path lengths of less than  $5 \times 10^{-3}$  cm. These path lengths were obtained by placing fused-silica inserts into 0.5-cm cells. Before each experiment, the cells were calibrated with alkaline chromate solutions. The absorption spectra were recorded on a Cary 14R spectrophotometer equipped with an aluminum core furnace.<sup>24</sup> The temperatures in the furnace were measured with chromel–alumel thermocouples (from Pyrotenax) calibrated at the freezing points of pure tin and lead. The methodology used for voltammetric measurements has been described previously.<sup>21</sup>

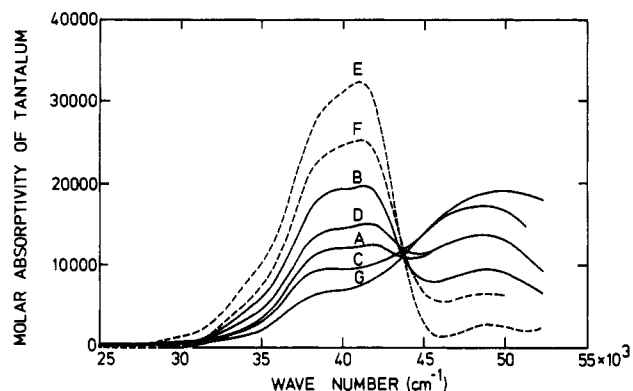
## Results and Discussion

**Potentiometric Measurements on NaCl–AlCl<sub>3</sub>–TaCl<sub>5</sub> Melts.** The values of the measured cell potential for different melt compositions (all containing 0.3 F TaCl<sub>5</sub>) at 175 °C are given in Table I. From the  $-\Delta E$  values in this table, the experimental average coordination number  $\bar{n}'$  (corrected for precipitation and the presence of oxo chloro complexes) could be calculated as a function of pCl. The results of these calculations are shown in Figure 1. It can be seen that at low pCl the average coordination number is close to 6. An average value of 6.00 (4) was obtained from the last four measurements in Table I. This result, when combined with the previously reported Raman spectra,<sup>6</sup> clearly indicates that Ta(V) is present as the complex ion TaCl<sub>6</sub><sup>-</sup> in melts of low pCl. When the pCl is increased,  $\bar{n}'$  drops below 6.0, which indicates the formation of Ta(V)–chloride species other than TaCl<sub>6</sub><sup>-</sup>. At even higher pCl values (greater than ca. 3.6), a white precipitate was observed in the melt. On the basis of the previously reported Raman spectra,<sup>6</sup> it is most likely that the Ta(V) species formed at higher pCl is either TaCl<sub>5</sub> or Ta<sub>2</sub>Cl<sub>10</sub> or a combination of these two. Consequently, hypotheses involving equilibria between TaCl<sub>6</sub><sup>-</sup> and TaCl<sub>5</sub> and Ta<sub>2</sub>Cl<sub>10</sub> and precipitates of solid TaCl<sub>5</sub> were tested using a computer program. This program was based on a non-linear least-squares regression analysis which calculated the average coordination numbers using the  $pK$  values for the equilibria between the different tantalum species as independent variables. In this way a minimum variance between measured and calculated  $\bar{n}'$  values was obtained for each model. In these calculations only the data given in Table I with  $-\Delta E$  values higher than 125 mV were used. The data with  $-\Delta E$  values of less than 125 mV are not useful for a discrimination between models because all models will have similar variances in this range.

The results of the computations are shown in Table II. The experimental variance can be calculated from the measurements where  $\bar{n}'$  theoretically should be equal to 6.00. Here a value of  $17.3 \times 10^{-4}$  was found. By the use of an  $F$  test<sup>11</sup> it is possible to distinguish between models which have a probability of either greater or less than 90%. Only models with a probability of greater than 90% were considered as being able to explain the potentiometric measurements; these models are marked with asterisks.



**Figure 2.** Ultraviolet-visible spectra of tantalum(V) in acidic melts. Spectra A and B are of measured solutions with the following mole fractions of NaCl and AlCl<sub>3</sub>, formal concentration of TaCl<sub>5</sub>, pCl, and  $\bar{n}'$ , respectively: (A) 0.4943, 0.5048, 0.0144, 4.46, 5.17; (B) 0.4941, 0.5046, 0.0219, 4.46, 5.19. In spectrum C the influence of oxide impurities has been eliminated by subtracting spectrum A from spectrum B. In spectrum D a further subtraction has removed the spectrum of TaCl<sub>6</sub><sup>-</sup>, giving the calculated spectrum of TaCl<sub>5</sub>.



**Figure 3.** Ultraviolet-visible spectra of tantalum(V) in basic melts. Spectra A–D and G are of measured solutions with the following mole fractions of NaCl and AlCl<sub>3</sub>, formal concentration of TaCl<sub>5</sub>, pCl, and  $\bar{n}'_{Ta(V)}$ , respectively: (A) 0.5029, 0.4962, 0.0141, 1.12, 5.99; (B) 0.5029, 0.4957, 0.0229, 1.12, 5.99; (C) 0.5031, 0.4960, 0.0144, 1.12, 5.99; (D) 0.5031, 0.4955, 0.0244, 1.12, 5.99; (G) 0.5014, 0.4938, 0.0243, 1.12, 3.99. The solution which gives rise to spectrum G has, besides NaCl, AlCl<sub>3</sub>, and TaCl<sub>5</sub>, an addition of Na<sub>2</sub>O (mole fraction 0.0033, or formality 0.0598). The average experimental coordination number for chloride ions is in this case close to 4 due to the formation of TaOCl<sub>4</sub><sup>-</sup>.

As may be seen from Table II, the only model that is not able to explain the measurements is the one where only Ta<sub>2</sub>Cl<sub>10</sub> is formed together with TaCl<sub>6</sub><sup>-</sup>.

### Spectrophotometric Measurements on NaCl–AlCl<sub>3</sub>–TaCl<sub>5</sub> Melts.

The spectra of tantalum(V) in slightly acidic melts at 175 °C are shown in Figure 2 (spectra A and B). In both spectra a small correction has been made for the amount of TaCl<sub>5</sub> present in the gas phase above the melt (see Appendix). The melt compositions correspond to pCl values of 4.46<sub>3</sub> and 4.46<sub>7</sub>, respectively. It should be noted that spectra A and B resemble each other closely. Since the concentrations of tantalum(V) differ in the two melts, it is reasonable to expect that the spectra are not much affected by oxide impurities present in the melts, because a constant oxide impurity will affect a low tantalum concentration more than a high tantalum concentration.

The influence of the oxide impurities can be further eliminated by subtracting the two spectra from each other and calculating the formal absorptivity of the difference as shown in spectrum C. Since the  $\bar{n}'$  value for tantalum(V) in solution is not 5 but 5.17–5.19, (i.e. TaCl<sub>6</sub><sup>-</sup> is also present), a further correction is necessary in order to obtain the spectrum of pure TaCl<sub>5</sub>. To perform this correction, the spectrum of pure TaCl<sub>6</sub><sup>-</sup> is needed. The spectrum of this complex is taken from Figure 3E and will be discussed below. Spectrum D (in Figure 2) is the result of this correction and should be the spectrum of pure TaCl<sub>5</sub>. It can be

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**Table III.** Band Maxima for TaCl<sub>6</sub><sup>-</sup>, NbCl<sub>6</sub><sup>-</sup>, and WCl<sub>6</sub> in UV-Visible Spectra [ $\nu_{\max}$ , 10<sup>3</sup> cm<sup>-1</sup> ( $\epsilon_{\max}$ , 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>)]

complex	NaCl–AlCl <sub>3</sub>		KCl–AlCl <sub>3</sub> 300 °C	gas phase 175 °C	MeEtimCl–AlCl <sub>3</sub>		acetonitrile room temp
	E = spectrum E F = spectrum F 175 °C				$\alpha$ = 51.0/49.0 mol % $\beta$ = 55.6/44.4 mol % room temp		
TaCl <sub>6</sub> <sup>-</sup>	E: 34.0 (sh), <sup>a</sup> 38.9 (sh), 41.1 (32.4), 49.0 (2.9) <sup>b</sup> F: 34.0 (sh), 38.9 (sh), 41.1 (25.2), 49.0 (6.5) <sup>b</sup>		31.8 (sh), 34.4 (26.3), 41.3 (6.7) <sup>f</sup>	27 (sh), 30.8 (23.7), 39.2 (7.4) <sup>h</sup>	$\alpha$ : 33.9 (6.3), 37.6 (23), 41.0 (31) <sup>c</sup> $\beta$ : 34.2 (7.5), 37.9 (24), 41.2 (31) <sup>c</sup>	34.8 (5.8), 38.0 (23.8), 41.5 (38.0), 49.5 (11.0) <sup>d</sup>	
NbCl <sub>6</sub> <sup>-</sup>	<i>e</i>					28.9 (sh <2.0), 31.8 (sh 11.4), 34.5 (28.9), 41.4 (6.4) <sup>d</sup>	
WCl <sub>6</sub>	27 (sh), 30.0 (13.0), ? <sup>g</sup>						

<sup>a</sup>sh = shoulder. <sup>b</sup>This work. <sup>c</sup>Reference 10. <sup>d</sup>Reference 25. <sup>e</sup>Not known. <sup>f</sup>Reference 11. <sup>g</sup>Reference 26. <sup>h</sup>Reference 27.

seen that TaCl<sub>5</sub> has two band maxima located at ca. 40.2 × 10<sup>3</sup> and 49.6 × 10<sup>3</sup> cm<sup>-1</sup>.

A comparison between the spectrum of TaCl<sub>5</sub> obtained in this work and the spectrum of NbCl<sub>5</sub> in KCl–AlCl<sub>3</sub> from previous work<sup>11</sup> shows that the bands of TaCl<sub>5</sub> are found at somewhat higher frequencies than the corresponding bands for NbCl<sub>5</sub> (which are located at 33.7 × 10<sup>3</sup> and 43.8 × 10<sup>3</sup> cm<sup>-1</sup>, respectively). The molar absorptivities of the TaCl<sub>5</sub> bands are also higher than the molar absorptivities of the corresponding NbCl<sub>5</sub> bands.

The spectra of tantalum(V) in a basic melt saturated with NaCl at 175 °C are shown in Figure 3 (spectra A–D). Under the given circumstances, we know from the potentiometric measurements that the average experimental coordination number for chloride is close to 6. Spectrum G (Figure 3) is also obtained from a saturated melt, but in this case an excess of Na<sub>2</sub>O has been added, converting TaCl<sub>6</sub><sup>-</sup> completely to TaOCl<sub>4</sub><sup>-</sup> (TaOCl<sub>4</sub><sup>-</sup> is distinguished from for example TaOCl<sub>5</sub><sup>2-</sup> by model discrimination<sup>16</sup>).

The chloride activity is the same for all spectra in Figure 3; therefore, the differences in the spectra must be due to different degrees of conversion to oxo chloro complexes. Furthermore, the spectra seem to form a (not very well defined) isosbestic point around 43.8 × 10<sup>3</sup> cm<sup>-1</sup>. This indicates, as expected,<sup>16</sup> the formation of only one oxide species together with TaCl<sub>6</sub><sup>-</sup>. The rather low quality of the isosbestic point is probably due to difficulties in obtaining a correct value for the path length of the melt and to a smaller extent due to the uncertainty in the concentration of the added tantalum(V). A further error results from the uncertainty in the amount of oxide impurity found in the TaCl<sub>5</sub> added. Spectra A and B have not been corrected for this oxide impurity (because an analysis showed it to be very small). However, in the case of spectra C, D, and G, such a correction has been performed. (It should be noted that the value for the oxide content used in this correction is determined indirectly from a chlorine analysis of TaCl<sub>5</sub>). In order to make a correction in spectra C and D, it is furthermore necessary to know the spectrum of the pure oxo species formed in NaCl-saturated solutions. Spectrum G represents such a spectrum, obtained when an excess of oxide is present.

Since spectra A and B are obtained from melts made from the same batch of chemicals, a subtraction of spectrum A from spectrum B should to a large extent remove the influence of the oxo chloro compound due to impurities in the melt (i.e. from AlOCl). The result of this subtraction (multiplied by the proper constant) is given as spectrum E, which should then be the spectrum of pure TaCl<sub>6</sub><sup>-</sup>. However, spectra C and D are also made with chemicals from the same batch and a similar subtraction procedure will in this case give spectrum F. It can be seen that there is a significant difference in molar absorptivities between spectra E and F. One explanation could be that our assumption about an equal concentration of oxide in each of the two sets of melts used to obtain spectra A and B and spectra C and D, respectively, is not correct.

It should be noted that even if there is a fairly large difference in the molar absorptivity between spectra E and F, the shapes of two spectra are similar (and the bands are at the same frequencies). Furthermore, since we are dealing with a two-species system, the possible maximum molar absorptivity of the main band located

around 41.1 × 10<sup>3</sup> cm<sup>-1</sup> cannot be much higher than found in spectrum E. A further increase in the absorptivity of this band (obtained for example by assuming higher amounts of oxide in the melt giving rise to spectrum B than in the melt giving rise to spectrum A) will result in negative values of the molar absorptivity in the wavenumber range above 46 × 10<sup>3</sup> cm<sup>-1</sup>. We can therefore conclude that spectrum E represents the upper limit for the absorptivity of the spectrum of TaCl<sub>6</sub><sup>-</sup>. It is not clear whether spectrum F represents the lower limit, but at least the molar absorptivity of the 41.1 × 10<sup>3</sup> cm<sup>-1</sup> band has to be higher than what is found in the case of spectrum B.

An inspection of spectrum E indicates that the two main bands of TaCl<sub>6</sub><sup>-</sup> are located at ca. 41.1 × 10<sup>3</sup> and ca. 49.0 × 10<sup>3</sup> cm<sup>-1</sup> with molar absorptivities of 32.4 × 10<sup>3</sup> and 2.9 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>, respectively. These band positions should be compared with the band positions found for TaCl<sub>6</sub><sup>-</sup> in basic MeEtimCl–AlCl<sub>3</sub><sup>24</sup> and in acetonitrile.<sup>25</sup> The band positions in these three media agree rather well with each other, as can be seen in Table III. In Table III is also shown a comparison with NbCl<sub>6</sub><sup>-</sup> in KCl–AlCl<sub>3</sub><sup>11</sup> and acetonitrile.<sup>25</sup> It can be seen that, in this case as well, there is a shift to higher band frequencies from niobium(V) to tantalum(V) whereas the molar absorptivities are rather similar. It should be noted further that a well-defined shoulder can be found in the spectrum of TaCl<sub>6</sub><sup>-</sup> around 38.9 × 10<sup>3</sup> cm<sup>-1</sup>. In the case of NbCl<sub>6</sub><sup>-</sup> in KCl–AlCl<sub>3</sub>,<sup>11</sup> this shoulder, which is not very pronounced, is found around 31.8 × 10<sup>3</sup> cm<sup>-1</sup>. It is also interesting to compare the spectrum of TaCl<sub>6</sub><sup>-</sup> with the spectrum of the isoelectronic complex WCl<sub>6</sub>. Because of oxo chloro formation, the spectrum of WCl<sub>6</sub> is not known with high accuracy in NaCl–AlCl<sub>3</sub> solutions.<sup>26</sup> It is however clear that the strongest band is located at 30.0 × 10<sup>3</sup> cm<sup>-1</sup> and a shoulder seems to be present around 27 × 10<sup>3</sup> cm<sup>-1</sup> whereas it is difficult to predict where the other main band is located. Contrary to this, the spectrum of WCl<sub>6</sub> is known fairly accurately in the gas phase.<sup>26,27</sup> The strongest band in this case is located at 30.8 × 10<sup>3</sup> cm<sup>-1</sup>, which is not far from the position in the NaCl–AlCl<sub>3</sub> melt. Therefore, there are reasons to believe that the other main band located at 39.2 × 10<sup>3</sup> cm<sup>-1</sup> in the gas phase has approximately the same position in NaCl–AlCl<sub>3</sub> melts.

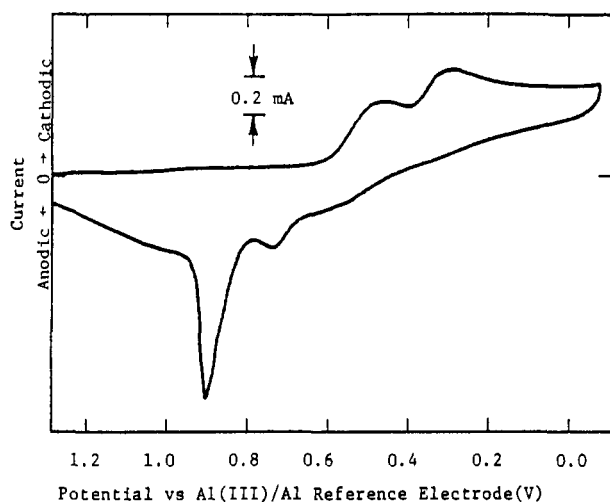
It can be seen that these band positions are far removed from the band positions in the spectrum of TaCl<sub>6</sub><sup>-</sup> in NaCl–AlCl<sub>3</sub>. This difference is probably due to the negative charge on the TaCl<sub>6</sub><sup>-</sup> complex. From Table III it can be seen that the molar absorptivity for the 30.0 × 10<sup>3</sup> cm<sup>-1</sup> band of WCl<sub>6</sub> in NaCl–AlCl<sub>3</sub> is somewhat lower than the molar absorptivity of the similar band for TaCl<sub>6</sub><sup>-</sup> in NaCl–AlCl<sub>3</sub> (whereas the molar absorptivities for WCl<sub>6</sub> in the gas phase are rather similar to the molar absorptivities of TaCl<sub>6</sub><sup>-</sup> in NaCl–AlCl<sub>3</sub>).

**Voltammetric Measurements of the Reduction of Ta(V) in NaCl–AlCl<sub>3</sub> Melts.** The redox chemistry of Ta(V) in several compositions of NaCl–AlCl<sub>3</sub> was studied using electrochemical methods. Studies in melts saturated with NaCl (pCl = 1.1) have

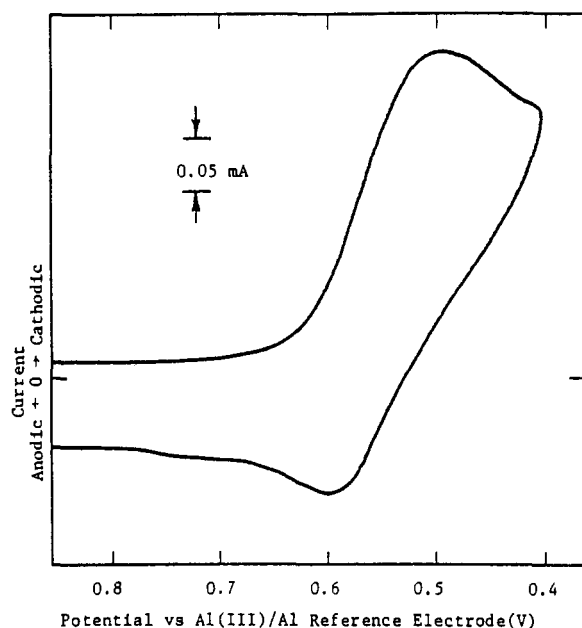
(25) Valloton, M.; Merbach, A. E. *Helv. Chim. Acta* 1974, 57, 2345.

(26) Schoebrechts, J.-P.; Flowers, P. A.; Hance, G. W.; Mamantov, G. J. *Electrochem. Soc.* 1988, 135, 3057.

(27) Takuma, T.; Kawakubo, S. *Nippon Kagaku Kaishi* 1972, 5, 865.



**Figure 4.** Cyclic voltammogram for the reduction of Ta(V) at a platinum electrode at 175 °C in NaCl-AlCl<sub>3</sub> (49–51 mol %): electrode area 0.09 cm<sup>2</sup>; Ta(V) concentration 3.05 × 10<sup>-2</sup> M; scan rate 0.1 V/s.

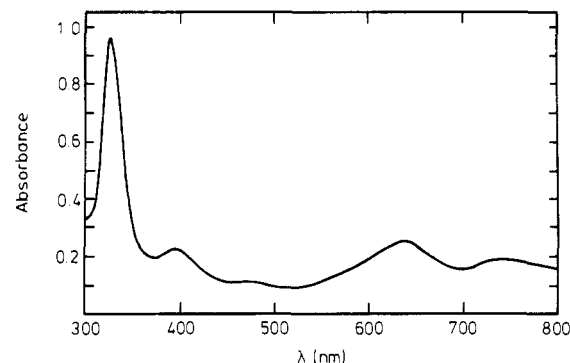


**Figure 5.** Cyclic voltammogram for the first reduction wave of Ta(V) at a platinum electrode at 160 °C in NaCl-AlCl<sub>3</sub> (49–51 mol %): electrode area 0.09 cm<sup>2</sup>; Ta(V) concentration 3.05 × 10<sup>-2</sup> M; scan rate 0.1 V/s.

dealt primarily with the differences in the electrochemical behaviors of TaCl<sub>6</sub><sup>-</sup> and TaOCl<sub>4</sub><sup>-</sup>. These studies have resulted in an electroanalytical method for the determination of dissolved oxide in these melts; this work has been reported previously.<sup>28</sup> The most conclusive results were obtained using the NaCl-AlCl<sub>3</sub> (49–51 mol % = 49/51) melt. Cyclic voltammetric studies were carried out in the 49/51 melt (pCl = 4.5) to examine the effect of scan rate, temperature, and Ta(V) concentration. A typical cyclic voltammogram (CV) for the overall reduction of Ta(V) at a Pt electrode at 175 °C and a scan rate of 0.1 V/s is shown in Figure 4. It may be seen that two reduction steps are involved. The CV for the first reduction step at 160 °C is relatively simple (Figure 5). The peak current for this reduction is proportional to the Ta(V) concentration, the current function ( $i_p/v^{1/2}$ ) is constant up to 1–2 V/s, and the peak current ratio ( $i_p^a/i_p^c$ ) approaches unity at faster scan rates (1–2 V/s). On the other hand, the peak potential  $E_p$  for the first reduction wave shifts anodically with increasing Ta(V) concentration. Such a shift provides ev-

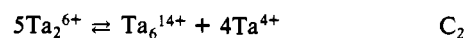
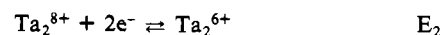
**Table IV.** Comparison between X-ray Powder Patterns for Ta<sub>6</sub>Cl<sub>14</sub>

$d, \text{Å}$		$d, \text{Å}$		$d, \text{Å}$	
this work	ref 31	this work	ref 31	this work	ref 31
8.59 s	8.58 s	2.72 m	2.70 m	2.03 w	
7.76 s	7.76 s	2.55 w		1.97 m	1.96 m
5.68 s	5.66 s	2.47 s	2.48 s	1.77 m	1.78 m
4.01 w		2.28 w		1.73 m	1.71 m
3.01 w	2.98 vw	2.22 w		1.56 w	
2.92 w		2.14 w	2.16 vw	1.52 w	
2.85 w		2.09 m	2.08 m		



**Figure 6.** Adsorption spectrum of the Ta(V) reduction product in NaCl-AlCl<sub>3</sub> (49–51 mol %) dissolved in deoxygenated water (path length 1 cm).

idence for dimerization occurring after the reversible charge transfer.<sup>29</sup> As expected,<sup>29</sup> the plot of  $E_p$  vs  $\log C_{\text{Ta(V)}}$  is linear. The theoretical slope of this plot of  $2.303RT/2nF$ ; an  $n$  value of 1.02 has been obtained from this plot. The second reduction step in Figure 4 is quite irreversible even at scan rates of 2 V/s. The sharp reoxidation peak at 0.9 V, observed only if the reduction is extended to the second step, is characteristic of the reoxidation of a deposit on the electrode. To learn more about the product of the second reduction step, a controlled-potential coulometric experiment was performed. The potential of the glassy-carbon cathode was controlled at 0.13 V (vs the Al(III) in the 37/63 melt/Al reference electrode). A dark green deposit was formed on the electrode surface. This deposit was removed from the electrode surface, filtered, and treated with molten AlCl<sub>3</sub> to remove any residual melt.<sup>30</sup> The X-ray powder pattern of the dark green powder was essentially identical to that of Ta<sub>6</sub>Cl<sub>14</sub><sup>31</sup> (see Table IV). The nonlinear  $\log i$  vs time plot for the electrolysis points in the direction of a catalytic or an ECE mechanism.<sup>32</sup> Although the  $n$  value obtained from electrolysis was 2.07, it is probably too low, since the current did not decay to background. The UV-visible spectrum of the pale green solidified melt used in the electrolysis and dissolved in deoxygenated water (see Figure 6) is identical to the spectrum of Ta<sub>6</sub>Cl<sub>12</sub><sup>2+</sup>.<sup>33</sup> The results summarized above point to the following reaction sequence for the reduction of Ta(V) in the 49/51 NaCl-AlCl<sub>3</sub> melt:



Although formation of metallic tantalum was not observed in the electrolysis, addition of aluminum to the green melt containing the tantalum cluster resulted, after 5 weeks at 175 °C, in bright

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(29) Saveant, J. M.; Vianello, E. *Electrochim. Acta* **1967**, *12*, 1545.

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(32) Meites, L. In *Techniques of Chemistry, Volume 1*; Weissberger, A., Rossiter, B. W., Eds.; Wiley-Interscience: New York, 1971; Part IIA, pp 645–712.

(33) Kuhn, P. J.; McCarley, R. E. *Inorg. Chem.* **1965**, *4*, 1482.

metallic particles which had an X-ray powder pattern identical to that of tantalum metal. The reduction of Ta<sub>6</sub>Cl<sub>14</sub> to tantalum in the 49/51 melt at 175 °C may be slow because of the low solubility of Ta<sub>6</sub>Cl<sub>14</sub> in the melt. It is not unlikely that the Ta<sub>6</sub>Cl<sub>14</sub> layer on the electrode surface blocks further reduction of tantalum in this melt.

### Conclusions

It has been shown that tantalum(V) forms two complexes, TaCl<sub>6</sub><sup>-</sup> and TaCl<sub>5</sub>, in basic and moderately acidic NaCl–AlCl<sub>3</sub> melts at 175 °C, respectively. These complexes have been characterized by their visible and ultraviolet spectra and by the p*K* value for the acid/base equilibrium between them at 175 °C. The existence of other complexes such as Ta<sub>2</sub>Cl<sub>10</sub> is not very likely but cannot be completely ruled out.

Solvation has not been examined in the present investigation, but it is possible that TaCl<sub>5</sub> reacts with AlCl<sub>3</sub> (or TaCl<sub>4</sub><sup>+</sup> with AlCl<sub>4</sub><sup>-</sup>), forming TaAlCl<sub>8</sub> in very acidic melts, similar to what has been found for NbCl<sub>5</sub>.<sup>34</sup> However, the experimental methods used are not suited for such an investigation. In the course of the present work, it was found to be very difficult to obtain spectra of the pure chloro complexes due to the high affinity of these complexes for oxide ions. TaCl<sub>5</sub> was extremely reactive in the gaseous phase (it reacted with the silica wall); therefore, it was not—in contrast to the case for NbCl<sub>5</sub>—possible to obtain the gas-phase spectrum of this compound. The electrochemical reduction of tantalum(V) in acidic alkali-metal chloroaluminate melts results in cluster formation. No tantalum metal was observed in the electrolysis.

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### Appendix

In order to examine the influence of TaCl<sub>5</sub> in the gas phase above the melt, two different considerations were made. One involved vapor pressure measurements from the literature; the other measurements involved the distribution coefficient between the gas phase and the liquid phase for TaCl<sub>5</sub>.

The vapor pressure of pure solid TaCl<sub>5</sub>, *P*<sub>(s)</sub>, has been measured by Sadoway and Flengas,<sup>35</sup> who found the following empirical equation:

$$\ln (P_{(s)}/\text{atm}) =$$

$$42.180 - 11123T^{-1} - 3.2207 \ln T - 1.761 \times 10^4 T^{-2}$$

(34) Krebs, B.; Janssen, H.; Bjerrum, N. J.; Berg, R. W.; Papatheodorou, G. N. *Inorg. Chem.* **1984**, *23*, 164.

(35) Sadoway, D. R.; Flengas, S. N. *Can. J. Chem.* **1976**, *54*, 1692.

which at a temperature of 175 °C gives

$$P_{\text{TaCl}_5(g)} = 0.0916 \text{ atm}$$

The highest concentration of TaCl<sub>5</sub> in the gas phase must be obtained when the melt is saturated with TaCl<sub>5</sub>. If we assume that no vapor complexes are formed, the pressure of TaCl<sub>5</sub> above the melt should be equal to the pressure above solid TaCl<sub>5</sub> at 175 °C.

The volume above the melt in the potentiometric cell is not more than 10 cm<sup>3</sup>. The ideal gas equation indicates in this case that 8.84 × 10<sup>-3</sup> g of TaCl<sub>5</sub> should be present in the gas phase. Since ca. 0.650 g of TaCl<sub>5</sub> was added to the potentiometric cell, this corresponds to only 1.4% of the total added TaCl<sub>5</sub>.

Another way to check the amount of TaCl<sub>5</sub> in the gas phase while allowing also for the formation of vapor complexes with Al<sub>2</sub>Cl<sub>6</sub> (from the solvent) is to use the distribution coefficient between the gas phase and the liquid phase. A few unfortunately not very accurate measurements have been made to obtain this value. An average of four measurements gave a value of 0.045 ± 0.013 for TaCl<sub>5</sub> in NaAlCl<sub>4</sub> (pCl range 4.13–4.57) at 175 °C.<sup>16</sup> This should be compared with a value of 0.133 ± 0.011 found for NbCl<sub>5</sub> in KAlCl<sub>4</sub> (pCl range 4.24–5.39) at 300 °C.<sup>11</sup> The main reason for the higher value in this latter case is probably the temperature. (The distribution coefficient (but not the vapor pressure) was found to be independent of pCl in the range studied.) The vapor pressure above the solid or liquid phase is higher for TaCl<sub>5</sub> than for NbCl<sub>5</sub> at the measured temperatures.<sup>35</sup> An average of three measurements gave a higher value (i.e. 0.99 ± 0.34) for the distribution coefficient for TaCl<sub>5</sub> at 300 °C<sup>28</sup> than for NbCl<sub>5</sub> at 300 °C.<sup>11</sup>

Since we know from the potentiometric measurements that the concentration of TaCl<sub>5</sub> in the TaCl<sub>5</sub>-saturated solution at 175 °C is close to 0.807 ± 0.09 M, we can calculate the amount in the gas phase above the melt in the potentiometric cell to be 10 × 10<sup>-3</sup> × 0.087 × 0.045 × *M*<sub>TaCl<sub>5</sub></sub> = 14.0 × 10<sup>-3</sup> g, which corresponds to 2.2% of the total amount of Ta(V). It can be seen that this value is not (the uncertainty taken into consideration) very different from the value calculated from the vapor pressure measurements. This does not, however, exclude the formation of vapor-phase complexes, especially at higher temperatures, where the vapor pressure of Al<sub>2</sub>Cl<sub>6</sub> above the melt is higher. Such vapor complexes have been found in connection with NbCl<sub>5</sub>.<sup>34</sup>

Because of the above consideration, no correction was made for the amount of TaCl<sub>5</sub> present above the melt in the potentiometric measurements. However, in the spectrophotometric cells, a correction is necessary because of the much smaller melt volume (ca. 3.2 cm<sup>3</sup>). It can be calculated that in the slightly acidic melts (spectra A and B) ca. 11.5% of all Ta(V) was found in the gas phase.

Registry No. Ta, 7440-25-7; NaCl, 7647-14-5; AlCl<sub>3</sub>, 7446-70-0; TaCl<sub>6</sub><sup>-</sup>, 21640-07-3; TaCl<sub>5</sub>, 7721-01-9.