Inorg. Chem. **2005**, *44*, 9847–9851

Inorganic Chemistry

Article

Electrochemical and Spectroscopic Studies of the Chloro and Oxochloro Complex Formation of Nb(V) and Ta(V) in NaCl–AlCl$_3$ Melts

J. H. von Barner* and N. J. Bjerrum

Department of Chemistry, Kemitorvet, Technical University of Denmark, DK-2800 Lyngby, Denmark

Received March 10, 2005

The equilibrium constant for the chloro complex formation of Nb(V)

$$NbCl_6^- \leftrightarrow NbCl_5 + Cl^- \qquad (i)$$

in NaCl–AlCl$_3$ melts at 175 °C was found to be pK_i = 2.86(5). The oxochloro complex formation of Nb(V) and Ta(V) in NaCl–AlCl$_3$ melts at 175 °C could be explained by the following equilibria:

$$MOCl_4^- \leftrightarrow MOCl_3 + Cl^- \qquad (ii)$$

$$MOCl_3 \leftrightarrow MOCl_2^+ + Cl^- \qquad (iii)$$

where M = Nb and Ta. The equilibrium constants determined by potentiometric measurements with chlorine–chloride electrodes were, for M = Nb, pK_{ii} = 2.21(4) and pK_{iii} = 3.95(5) and, for M = Ta, pK_{ii} = 2.743(15) and pK_{iii} = 4.521(13). NbCl$_6^-$ has two bands in the UV–vis region, a strong one at 34.7 × 10^3 cm^{-1} and a weaker one at 41.6 × 10^3 cm^{-1}. The MOCl$_4^-$ complexes showed in the case of Nb(V) absorption bands at 32.7 and 42.9 × 10^3 cm^{-1} and in the case of Ta(V) at 38.6 and 48.1 × 10^3 cm^{-1}.

Introduction

Electrodeposition of niobium and tantalum from molten halide solvents has been the subject of numerous investigations. In general, fluoride mixtures seem to be the most favorable supporting liquids from a deposition point of view. However, because fluoride melts are very aggressive and may also have unwanted environmental effects, much research has been focused on the use of various chloride melts as solvents for plating processes. However, niobium and tantalum have in chloride melts a tendency to form insoluble lower valent cluster compounds, disturbing the plating process. Despite this, it has, for example, been possible to deposit Al–Nb alloys from a low-melting chloroaluminate electrolyte.[1] Thus such melts may be interesting candidates as solvents for deposition of niobium and tantalum.

Knowledge about the species formed by the metals to be deposited is essential in order to design proper plating processes. Both NbCl$_5$ and TaCl$_5$ are Lewis acids forming MCl$_6^-$ complexes when sufficient amounts of free chloride ions are present. We have previously reported results on the chloro complex formation of Nb(V) in KCl–AlCl$_3$ melts[2] at 300 °C and of Ta(V) in NaCl–AlCl$_3$ melts[3] at 175 °C by potentiometric and spectrophotometric measurements. It was obvious[2,3] that the niobium and tantalum chloro complexes would react with oxide ions originating from impurities in the salts that made up the melts or from contact with water vapor, resulting in the formation of oxochloro species. Indeed, oxide impurities often cause serious problems when depositing niobium and tantalum from halide melts, disturbing the electrochemical reduction and giving impure deposits of the metals.[4] In the solid state, the existence of the complex ion NbOCl$_5^{2-}$ has been demonstrated[5] by Raman and IR spectroscopy and by X-ray diffraction studies on [As(C$_6$H$_5$)$_4$]$_2$NbOCl$_5$·2CH$_2$Cl$_2$ and it is also known[6] to be present in solid RbNbOCl$_5$ and CsNbOCl$_5$. In solution,

---

* To whom correspondence should be addressed. E-mail: jvb@kemi.dtu.dk.

(1) Stafford, C. R.; Haarberg, G. M. *Plasmas Ions* **1999**, *1*, 35.

(2) von Barner, J. H.; Bjerrum, N. J.; Smith, G. P. *Acta Chem. Scand.* **1978**, *A32*, 827.

(3) von Barner, J. H.; McCurry, L. E.; Jørgensen, C. A.; Bjerrum, N. J.; Mamantov, G. *Inorg. Chem.* **1992**, *31*, 1034.

(4) Gillesberg, B.; von Barner, J. H.; Bjerrum, N. J.; Lantelme, F. *J. Appl. Electrochem.* **1999**, *29*, 934.

(5) Müller, U.; Lorenz, I. *Z. Anorg. Allg. Chem.* **1980**, *463*, 110.

(6) Sabatini, A.; Bertini, I. *Inorg. Chem.* **1966**, *5*, 204.

10.1021/ic050367a CCC: $30.25

$NbOCl_5^{2-}$ has been identified in hydrochloric acid,[7] in various nonaqueous solvents,[8,9] and in CsCl−$NbOCl_3$ melts with CsCl in excess.[10] $NbOCl_4^-$ ions formed in the latter melts[10] when less CsCl was added, and the presence of this complex was also indicated in acetonitrile[8,9] and dioxane[9] solutions. Concerning Ta(V), oxochloro species of types similar to the ones for Nb(V) formed in CsCl−$TaOCl_3$ melts.[11]

Because the equilibrium constants for the chloro complex formation of Nb(V) in NaCl−$AlCl_3$ melts have not previously been determined, we decided to investigate this especially at low temperature (i.e., 175 °C). However, the main focus of the present work is to clarify which oxochloro complexes, niobium or tantalum, will form in NaCl−$AlCl_3$ melts.

Experimental Section

$AlCl_3$ was prepared at 700 °C by reaction between molten aluminum (99.999% from Atomergic Chemetals Corp.) and dry hydrogen chloride gas. Anhydrous NaCl was made by treating an analytical-grade material in the molten state with dry HCl gas. Details about the preparation of these salts, which made up the solvent, have been given in a previous paper.[12]

AlOCl was applied as the oxide source. It was synthesized by the reaction between V_2O_5 and $AlCl_3$. The latter chemical was added in an amount approximately 10 times greater than that of V_2O_5. After reaction, $VOCl_3$ and the excess of $AlCl_3$ were distilled off at 300 °C. The final AlOCl had a chloride content of 44.9_7% (determined by Volhard titration) compared to a calculated content of 45.0%. $NbCl_5$ was made by the reaction of metallic niobium (99.99% from Schuchardt) with chlorine gas (99.9% from Fluka) at 600 °C. The product was purified by 5 times successive sublimation under chlorine (0.33 atm). $TaCl_5$ (99.9% from Fluka) was similarly sublimed at 200 °C.

The chlorine-chloride concentration cells for the potentiometric measurements have been described in detail elsewhere.[13] The apparatus and optical cells applied in the spectrophotometric experiments were of the same type as that in our previous work.[3] The Raman spectra were recorded with the same instrumentation as was previously used[14] and were obtained from melts contained in Pyrex ampules sealed under argon.

The program used for testing of the different model equilibria was similar to the one applied before.[13]

Definitions and Assumptions

In the calculations, it has been assumed that AlOCl reacts quantitatively with the pentachlorides of niobium and tantalum, i.e., according to

$$MCl_5 + AlOCl \rightarrow MOCl_3 + AlCl_3 \qquad (1)$$

where M = Nb and Ta.

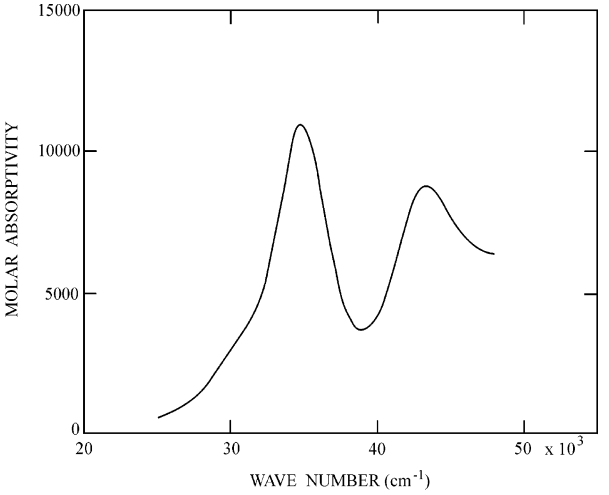

Figure 1. UV−vis gas-phase spectrum of $NbCl_5$ at 300 °C.

From our previous work[3] on Ta(V) in NaCl−$AlCl_3$, we know from UV−vis spectra that oxide addition completely converts $TaCl_6^-$ to an oxochloro complex, and as we shall see later, both Raman and UV−vis spectroscopic measurements support this assumption also for niobium.

The measurements at 175 °C were not corrected for vaporization of niobium or tantalum species into the gas phase over the melt. In the previous work,[3] this situation with $TaCl_5$ dissolved in NaCl−$AlCl_3$ melts was considered. For potentiometric measurements performed in a similar pCl^- region as that in the present work, it was concluded that no correction for vaporization of $TaCl_5$ was needed at 175 °C. Concerning niobium, we have previously[2] measured the gas-phase spectrum of pure $NbCl_5$ at 300 °C. Unfortunately, during the calculation of the molar absorptivities, the measured spectrum was multiplied with a wrong factor. Thus, the intensities on the spectrum in ref 2, Figure 4A, became to high by a factor of 1.822. The correct spectrum for gaseous $NbCl_5$ at 300 °C is given in Figure 1. As can be seen, maximum absorbance occurs at 35×10^3 cm^{-1} (286 nm). At this wavelength, only a slightly visible shoulder appeared on the vapor-phase spectrum above a NaCl−$AlCl_3$ melt with $NbCl_5$ added (average chloride coordination number of approximately 5.5) at 175 °C. This implies for our experiments that less than 1% of the added $NbCl_5$ will be present in the vapor phase at this temperature. Like in the case for KCl−$AlCl_3$ melts,[2] the vaporization of $NbCl_5$ from acidic NaCl−$AlCl_3$ melts at 300 °C was not negligible. For the latter solvent, we estimate, from a spectrophotometric measurement, the vapor−liquid distribution coefficient for $NbCl_5$ to be 0.03 at 300 °C.

Our $AlCl_3$ often contained a minor impurity of AlOCl. This amount of AlOCl can be calculated from a potentiometric measurement on the equimolar NaCl−$AlCl_3$ solvent as described previously.[13] Such a measurement was always performed before the addition of the solutes, and the $AlCl_3$ amounts referred to in this work are the corrected ones. The calculations of the average coordination numbers and the equilibrium constants are performed with assumptions for the solvent and the electrochemical cell similar to those we used before.[3] Because we assume a total reaction between

---

(7) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1967**, 675.
(8) Furlani, C.; Zinato, E. *Z. Anorg. Allg. Chem.* **1967**, *351*, 210.
(9) Miranda, C.; da Silveira, M.; Vernois, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 839.
(10) Rosenkilde, C.; Voyiatzis, G. A.; Jensen, V. R.; Ystenes, M.; Østvold, T. *Inorg. Chem.* **1995**, *34*, 4360.
(11) Rosenkilde, C.; Voyiatzis, G. A.; Østwold, T. *Acta Chem. Scand.* **1995**, *49*, 405.
(12) Hjuler, H. A.; Mahan, A.; von Barner, J. H.; Bjerrum, N. J. *Inorg. Chem.* **1982**, *21*, 402.
(13) Zachariassen, K.; Berg, R. W.; Bjerrum, N. J.; von Barner, J. H. *J. Electrochem. Soc.* **1987**, *134*, 1153.
(14) Bjerrum, N. J.; Berg, R. W.; Christensen, E.; Kerridge, D. H.; von Barner, J. H. *Anal. Chem.* **1995**, *34*, 2129.

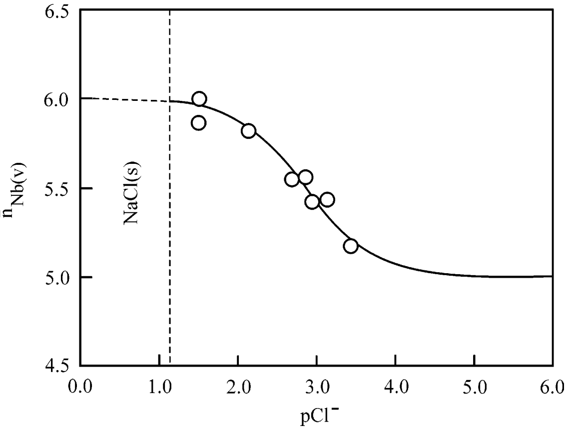

Figure 2. Average chloride coordination number as a function of pCl^- for a 0.08 M $NbCl_5$ solution in $NaCl-AlCl_3$ melts at 175 °C.

oxide and the added MCl_5, we apply the MO^{3+} entity as the basis for the average coordination numbers (M = Nb, Ta). Thus

$$\bar{n}_{MO^{3+}} = (C'_{NaCl} + 3C'_{AlCl_3} + 5C'_{MCl_5} + C'_{AlOCl} - 4[AlCl_4^-] - 7[Al_2Cl_7^-] - 10[Al_3Cl_{10}^-] - 6[Al_2Cl_6] - [Cl^-])/C'_{MCl_5} \quad (2)$$

where C' values are the formal concentrations of each of the added substances, i.e., the initial molar amounts dissolved in 1 L of the melt. Square brackets symbolize real molar concentrations. In the present work, the $NaCl-AlCl_3$ solvent melts have a composition near 1:1. In this case, it has been shown[12] that the cell potential is given by

$$\Delta E = (-RT/F)\ \ln([Cl^-_{II}]/[Cl^-_{I}]) \quad (3)$$

where I and II refer to the measuring and reference compartments, respectively. Thus, the pCl^- of the melt in the measuring compartment can be calculated from

$$pCl^-_{I} = -[F/(RT \ln 10)]\Delta E + pCl^-_{II} \quad (4)$$

where pCl^-_{II} is the pCl^- of the $NaCl-AlCl_3$ melt saturated with NaCl used as the reference electrode. At 175 °C, the value of pCl^-_{II} has been determined[15] to be 1.128.

Results and Discussion

$NbCl_5$ in $NaCl-AlCl_3$. The results of our potentiometric measurements with chlorine−chloride electrodes on 0.08 M $NbCl_5$ solutions at 175 °C can be seen in Figure 2, where the average chloride coordination numbers are plotted against pCl^-. As was the case for $NbCl_5$ in $KCl-AlCl_3$ melts,[2] the measurements could best be explained by the equilibrium

$$NbCl_6^- \leftrightarrow NbCl_5 + Cl^- \quad (5)$$

In the calculations, only the six experimental points with pCl values greater than 2 are used. Data with smaller pCl are not useful for model discrimination because all of the tested models give similar variances in this range.

Table 1. p*K* Values and Variances for Different Models of Chloro Complex Formation of Nb(V) in $NaCl-AlCl_3$ Melts at 175 °C[a]

	equilibria	pK_1	pK_2	variance $\times 10^4$
1.	$NbCl_6^- \leftrightarrow NbCl_5 + Cl^-$	2.86 (0.05)		33.06
2.	$2NbCl_6^- \leftrightarrow Nb_2Cl_{10} + 2Cl^-$	4.60 (0.13)		91.94
3.	$NbCl_6^- \leftrightarrow NbCl_5 + Cl^-$ $2NbCl_5 \leftrightarrow Nb_2Cl_{10}$	2.9 (0.10)	0.08 (2.4)	44.89
4.	$2NbCl_6^- \leftrightarrow Nb_2Cl_{11}^- + Cl^-$ $Nb_2Cl_{11}^- \leftrightarrow Nb_2Cl_{10} + Cl^-$	1.5 (0.3)	2.9 (0.2)	40.83
5.	$2NbCl_6^- \leftrightarrow Nb_2Cl_{11}^- + Cl^-$ $Nb_2Cl_{11}^- \leftrightarrow 2NbCl_5 + Cl^-$	2.3 (0.8)	3.4 (0.8)	37.67

[a] Number of measurements: 6.

As it appears from Table 1, other models besides $NbCl_5$, including Nb_2Cl_{10} and $Nb_2Cl_{11}^-$, cannot be ruled out on the basis of an *F* test at the 90% confidence level. However, from Raman spectroscopic experiments,[16] it does not seem likely that $Nb_2Cl_{11}^-$ is formed, whereas Nb_2Cl_{10} may well be present. Anyhow, including this species does not change the p*K* value for eq 5 much. From our measurements, it could be calculated to be 2.86 (±0.05) at 175 °C. This compares to a value of 3.89 (±0.04) for the corresponding equilibrium with tantalum in $NaCl-AlCl_3$ at the same temperature,[3] indicating that $TaCl_6^-$ under these circumstances, as expected (because of more binding electrons), is a more stable complex than $NbCl_6^-$.

In $KCl-AlCl_3$ melts, we previously found[2] a p*K* value of 4.49 for eq 5 for a 0.1 M solution of $NbCl_5$ but at a higher temperature (300 °C). To get an idea about the magnitude of the equilibrium constant at 300 °C in the $NaCl-AlCl_3$ solvent, we performed five measurements at 300 °C, with average coordination numbers ranging between 5.24 and 5.72. As at 175 °C, the coordination number increased with decreasing pCl^-. If we assume eq 5 to be valid, a p*K* value of 1.9 could be estimated at 300 °C. Thus, it seems that $NbCl_6^-$ under similar conditions is more stable in $KCl-AlCl_3$ melts than in $NaCl-AlCl_3$ melts because of the generally higher chloride activity in the former solvent. When we compare the equilibrium constants in the $NaCl-AlCl_3$ melts at the two temperatures, it is clear that an increase in temperature destabilizes $NbCl_6^-$; i.e., eq 5 is shifted to the right with an increase in temperature. This is, of course, what should be expected.

We also recorded the Raman spectrum of $NbCl_5$ dissolved in a $NaCl-AlCl_3$ melt saturated with NaCl at 175 °C. Besides the bands from $AlCl_4^-$, a polarized band appeared at 398 cm^{-1}. We assign this band to the symmetrical stretch vibration of $NbCl_6^-$, in agreement with the work of Huglen et al.[16]

Oxochloro Complexes, Potentiometric Measurements. The result of the potentiometric measurements can be seen in Figure 3, where the average coordination numbers ($\bar{n}$) for NbO^{3+} are plotted against pCl^- for a 0.10 M solution of $NbOCl_3$ in $NaCl-AlCl_3$ at 175 °C. It can be noticed that the average coordination number approaches 4 at low pCl^- values (i.e., basic melts). When the free chloride ion activity

---

(15) Fehrmann, R.; von Barner, J. H.; Bjerrum, N. J.; Nielsen, O. F. *Inorg. Chem.* **1981**, *20*, 1712.

(16) Huglen, R.; Mamantov, G.; Smith, G. P.; Begun, G. M. *J. Raman Spectrosc.* **1979**, *8*, 326.

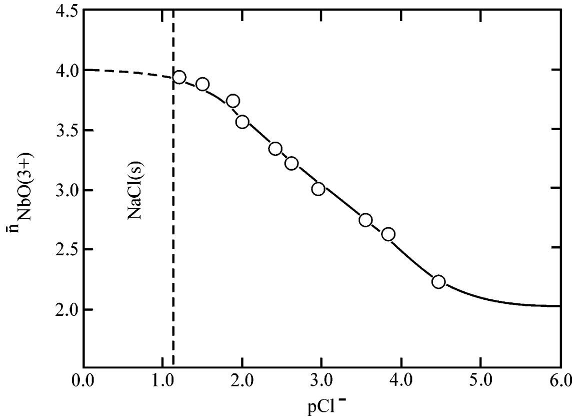

Figure 3. Average chloride coordination number as a function of pCl$^-$ for a 0.1 M $NbOCl_3$ solution in NaCl$-$AlCl$_3$ melts at 175 ° C.

Table 2. p*K* Values and Variances for Different Models of Oxochloro Complex Formation of Nb(V) in NaCl$-$AlCl$_3$ Melts at 175 °C[a]

	equilibria	pK_1	pK_2	variance × 10^4
1.	$NbOCl_4^- \leftrightarrow NbOCl_2^+ + 2Cl^-$	5.63 (25)		1521
2.	$NbOCl_4^- \leftrightarrow NbOCl_3 + Cl^-$ $NbOCl_3 \leftrightarrow NbOCl_2^+ + Cl^-$	2.207 (39)	3.95 (5)	18.83*
3.	$NbOCl_4^- \leftrightarrow NbOCl_3 + Cl^-$ $2NbOCl_3 \leftrightarrow (NbOCl_2)_2^{2+} + 2Cl^-$	2.16 (16)	6.81 (12)	49.99
4.	$2NbOCl_4^- \leftrightarrow (NbOCl_3)_2 + 2Cl^-$ $(NbOCl_3)_2 \leftrightarrow 2NbOCl_2^+ + 2Cl^-$	3.31 (7)	8.99 (10)	23.07*
5.	$2NbOCl_4^- \leftrightarrow (NbOCl_3)_2 + 2Cl^-$ $(NbOCl_3)_2 \leftrightarrow (NbOCl_2)_2^{2+} + 2Cl^-$	3.26 (12)	7.82 (12)	66.24

[a] Number of measurements: 10 (number of different cells: 2). Asterisks indicate those based on $F_{0.10}$ (8.8) = 2.59.

is diminished (i.e., increasing pCl$^-$ values), the average chloride coordination number drops, and in the most acidic melts, it gets close to 2. This certainly points in the direction of the formation of several oxochloro complexes. It seems obvious to suggest that $NbOCl_4^-$ is formed at low pCl$^-$ because the average coordination number for NbO^{3+} does not exceed 4. This is somewhat surprising because it is known from Raman spectroscopic measurements[10] that $NbOCl_5^{2-}$ is present in a number of alkali chloride melts with $NbOCl_3$ added. However, in the melts where $NbOCl_5^{2-}$ was observed, a larger excess of free chloride was present than in our case. The samples were typically mixtures of AlkCl$-$NbOCl$_3$ (Alk = alkali metal) with X_{AlkCl} greater than 0.66 or diluted solutions of $NbOCl_3$ in binary alkali chloride mixtures.[10]

Indeed, $NbOCl_4^-$ complexes have previously been identified by vibrational spectroscopy[17,18] in the solid state and were recently also observed in alkali chloride melts where only limited amounts of chloride were present.[10] Thus, models involving $NbOCl_4^-$ and various $NbOCl_x^{(x-3)-}$ species were tested. For the same reason as was mentioned in the previous chapter, only the eight most acidic measurements were used for model discrimination. Both monomeric and dimeric species were taken into account. In Table 2, the equilibria that could best explain our potentiometric measurements are shown. The models marked with an asterisk are the ones that have a probability greater than 90% (based on an *F* test). It seems clear that models involving two equilibria can best explain the experiments. Further, the two models with monomeric $NbOCl_2^+$ are clearly better than those with the corresponding dimeric species, i.e., $(NbOCl_2)_2^{2+}$. However, concerning $NbOCl_3$, we cannot distinguish between the monomeric and dimeric forms of this species.

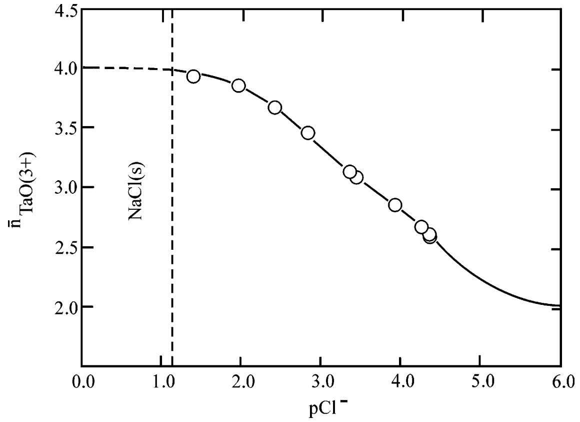

Figure 4. Average chloride coordination number as a function of pCl$^-$ for a 0.3 M $TaOCl_3$ solution in NaCl$-$AlCl$_3$ melts at 175 °C.

Table 3. p*K* Values and Variances for Different Models of Oxochoro Complex Formation of Ta(V) in NaCl$-$AlCl$_3$ Melts at 175 °C[a]

	equilibria	pK_1	pK_2	variance × 10^4
1.	$TaOCl_4^- \leftrightarrow TaOCl_2^+ + 2Cl^-$	7.1 (3)		1971
2.	$TaOCl_4^- \leftrightarrow TaOCl_3 + Cl^-$ $TaOCl_3 \leftrightarrow TaOCl_2^+ + Cl^-$	2.743 (15)	4.521 (13)	2.0*
3.	$TaOCl_4^- \leftrightarrow TaOCl_3 + Cl^-$ $2TaOCl_3 \leftrightarrow (TaOCl_2)_2^{2+} + 2Cl^-$	2.68 (4)	8.35 (4)	12.5
4.	$2TaOCl_4^- \leftrightarrow (TaOCl_3)_2 + 2Cl^-$ $(TaOCl_3)_2 \leftrightarrow 2TaOCl_2^+ + 2Cl^-$	4.86 (10)	9.53 (9)	28.1
5.	$2TaOCl_4^- \leftrightarrow (TaOCl_3)_2 + 2Cl^-$ $(TaOCl_3)_2 \leftrightarrow (TaOCl_2)_2^{2+} + 2Cl^-$	4.77 (11)	8.83 (6)	33.7

[a] Number of measurements: 10 (number of different cells: 2). Asterisks indicate those based on $F_{0.10}$ (8.8) = 2.59.

The average coordination numbers for TaO^{3+} as a function of pCl$^-$ based on potentiometric measurements on NaCl$-$AlCl$_3$ melts with $TaCl_5$ and AlOCl added can be seen in Figure 4. Also in this case, the average coordination number approaches 4 at low pCl$^-$. When the melts are made more acidic, i.e., with increasing pCl$^-$, the $\bar{n}$ values gradually diminish and reach values of around 2.5 for the most acidic melts investigated. It therefore seems reasonable to suggest that $TaOCl_4^-$ is formed in the basic melts. Consequently, we have, using the eight measurements with the highest pCl, tested models that involve this complex and one or two more tantulum(V) oxochloro complexes with Cl/Ta atomic ratios of less than 4. The result appears in Table 3. As can be seen from this table, only model 2, which involves two equilibria between the monomeric species $TaOCl_4^-$, $TaOCl_3$, and $TaOCl_2^+$, is able to explain the measurements on a 90% confidence level.

Spectroscopic Investigations. The UV$-$vis spectra of $NbCl_5$ dissolved in NaCl$-$AlCl$_3$ melts saturated with NaCl with and without oxide added have been recorded at 175 °C. To eliminate the influence of oxide impurities, two

---

(17) Hiller, W.; Strähler, J.; Prinz, H.; Dehnicke, K. *Z. Naturforsch.* **1984**, *39b*, 107.

(18) Morozov, I. S.; Lipatova, N. P. *Russ. J. Inorg. Chem.* **1968**, *13*, 1101.

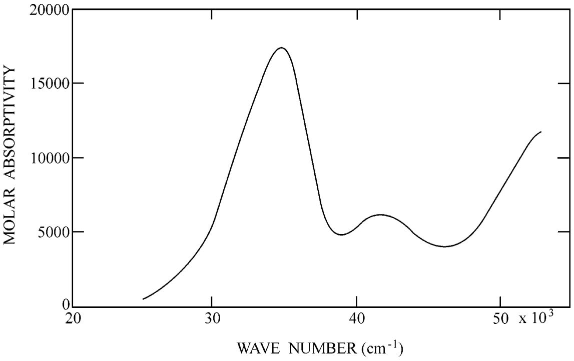

Figure 5. UV−vis spectrum of $NbCl_6^-$ in a basic NaCl−$AlCl_3$ melt (pCl^- = 1.12_8) at 175 °C. The spectrum is the result of a subtraction of two spectra with Nb(V) concentrations of 0.042 and 0.028 M, respectively.

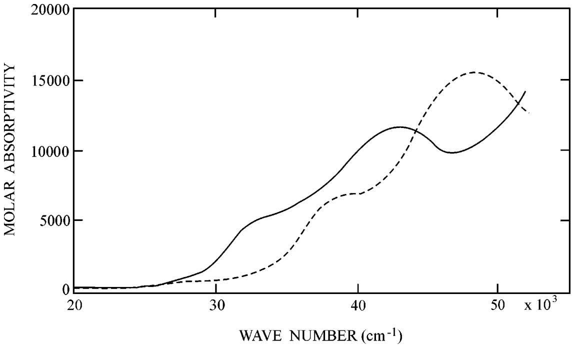

Figure 6. UV−vis spectra of $MOCl_4^-$ complexes (M = Nb, Ta) in basic NaCl−$AlCl_3$ melts (pCl = 1.12_8) at 175 °C. Full line: $NbOCl_4^-$. Dotted line: $TaOCl_4^-$.

spectra of melts prepared from the same batch of chemicals but with different amounts of $NbCl_5$ added were recorded. The spectrum shown in Figure 5 was obtained by subtraction of these. It has two bands, with the strongest band appearing at 34.7 × 10^3 cm^{-1} and a minor band at 41.6 × 10^3 cm^{-1}. We suggest that this spectrum arises from $NbCl_6^-$ in NaCl−$AlCl_3$. It is quite similar to the spectrum of $NbCl_6^-$ in KCl−$AlCl_3$ at 300 °C, for which we previously[2] observed bands at 34.4 and 41.3 × 10^3 cm^{-1}, with the former being by far the most intensive. Further, the spectrum of $TaCl_6^-$ in NaCl−$AlCl_3$ at 175 °C resembles the one of $NbCl_6^-$ in shape, but the bands appear at higher wavenumbers. In this case, the two main bands were found[3] at 41.1 and 49.0 × 10^3 cm^{-1}, and again the low-frequency band was the strongest.

Concerning the Raman spectrum, the band at 298 cm^{-1} disappeared when AlOCl was added to the $NbCl_5$−$NaCl_{sat}$−$AlCl_3$ melt in such an amount that the molar ratio of O/Nb became 1. This clearly indicates that $NbCl_6^-$ reacts with oxide, i.e., supporting our assumption of quantitative formation of an oxochloro species.

Also, the UV−vis spectrum changes considerately when oxide is added. The spectrum of $NbCl_5$ in a $NaCl_{sat}$−$AlCl_3$ melt with oxide added (O/Nb = 1) can be seen in Figure 6 (full line). Like the spectrum of $NbCl_6^-$, it has two bands, but they appear now at 32.7 and 42.9 × 10^3 cm^{-1}, respectively. Further, the intensity ratio has changed: the band with the highest wavenumber is now the most intense. The spectrum of the corresponding tantalum oxochloro species formed in NaCl−$AlCl_3$ melts saturated with NaCl is also shown in Figure 5 (dotted line). When we compare the spectra of the niobium(V) and tantalum(V) oxochloro species, it is seen that they resemble each other in shape, but the two bands on the tantalum spectrum are shifted toward higher wavenumbers. They appear at 38.6 and 48.1 × 10^3 cm^{-1}, respectively. As in the case of niobium, the spectrum is much different from the one of the chloro complex formed in the NaCl−$AlCl_3$ melt saturated with NaCl, i.e., $TaCl_6^-$, for which we previously[3] found the strongest band at 41.1 × 10^3 cm^{-1}. For NaCl−$AlCl_3$ melts saturated with NaCl, we know from our potentiometric measurements on samples with oxide added that the average chloride coordination number for MO^{3+} is 4 in the case of both M = Nb and M = Ta. Thus, the spectra shown in Figure 6 should arise from the pure $MOCl_4^-$ complexes.

Conclusions

It has been shown that $NbCl_6^-$ exists in basic NaCl−$AlCl_3$ melts at 175 °C. In moderately acidic melts, $NbCl_5$ is formed in equilibrium with $NbCl_6^-$, but the existence of other species such as Nb_2Cl_{10} cannot be completely ruled out. When oxide is added to NaCl−$AlCl_3$ melts with MCl_5 (M = Nb, Ta) dissolved, $MOCl_4^-$ complexes are formed in the basic melts. When the melts are made progressively more acidic, species of the types $MOCl_3$ and $MOCl_2^+$ appear. On the basis of potentiometric measurements, the equilibrium constants for the niobium(V) chloro and for the niobium(V) and tantalum(V) oxochloro complex equilibria in NaCl−$AlCl_3$ melts have been calculated. The UV−vis spectra of $NbCl_6$, $NbOCl_4^-$, and $TaOCl_4^-$ have also been obtained. It is found that under similar conditions Ta(V) forms stronger chloro and oxochloro complexes than Nb(V). The chloro complexes are more stable (at the same temperature) in KCl−$AlCl_3$ melts than in NaCl−$AlCl_3$ melts. Increasing the temperature from 175 to 300 °C (with the same solvent) will destabilize the higher chloro complexes.

Acknowledgment. We acknowledge Rolf W. Berg for recording the Raman spectra and Claus A. Jørgensen for assistance with the experiments.

IC050367A