XAFS STUDIES OF Ni, Ta AND Nb CHLORIDES IN THE IONIC LIQUID 1-ETHYL-3-METHYL IMIDAZOLIUM CHLORIDE / ALUMINUM CHLORIDE

W. E. O’Grady¹, D. F. Roeper¹,², K. I. Pandya³ and G. T. Cheek⁴

¹ Naval Research Laboratory, Code 6130, Washington, DC 20375
² EXCET, Inc., Springfield, VA
³ SAIC, Brookhaven National Laboratory, Upton, NY 11973
⁴ Chemistry Department, US Naval Academy, Annapolis, MD 21402

ABSTRACT
The structure of anhydrous nickel, niobium and tantalum metal chlorides in ionic liquids (IL) is important in the development of new electrochemical alloy deposition techniques. In order to understand the interactions of these metal ions with ionic liquids, we have investigated their structures in situ with X-ray Absorption Spectroscopy (XAS). The ionic liquid used in this study is 1-methyl-3-ethylimidazolium chloride (EMIC)/aluminum chloride (AlCl₃) and is formed by the addition of the Lewis acid AlCl₃ to the EMIC. The acid-base character of the IL can be changed by varying the ratio of the AlCl₃ to EMIC and thus changing the concentration of Cl⁻. This dramatically changes the structure of species formed when the metal chlorides dissolve in the solution. The coordination of NiCl₂ changes from tetrahedral in basic solution to octahedral in acidic solution. The NiCl₂ is also a stronger Lewis acid in that it can induce the aluminum chloride to share its chlorides in the strong acid solution forming a structure with six near Cl⁻ ions and 8 further away Al ions which share all the Cl⁻ ions surrounding the Ni²⁺. When Nb₂Cl₁₀, a dimer, is added to the acidic or basic solution, the dimer breaks up and forms two species. In the acid solution, two trigonal bipyramids are formed with five equal chloride distances while in the basic solution, a square pyramid with four chlorides forming a square base and one shorter axial chloride bond. Ta₂Cl₁₀ is also a dimer and breaks in half in the acidic solution and forms two trigonal bipyramids. However, in the basic solution the dimer divides in half but the specie formed is sufficiently acidic that it attracts two additional chloride ions and forms a seven coordinated tantalum specie.
INTRODUCTION

Our initial interest in the electrodeposition of metals and in particular niobium arose out of its superconducting properties and their use in the construction of RF cavities for free electron lasers. Electroplating of Nb has been called the “holy grail” by the designers of RF cavities for free electron lasers (Hand 2006). Also, Nb and Ta are both ingredients in alloys of significant importance to the Navy and possible new methods for repairing these materials in the field are of interest. Neither Nb nor Ta metals can be electroplated from aqueous solutions because the electrochemical potential for depositing these metals falls outside the window of electrochemical stability for water. However, using ionic liquids (ILs) for the electrodeposition of Nb and Ta is an appealing possibility because of their much larger range of potential stability, 2 to 3V compared to the 1.2 V of water. In order to become familiar with the details of using ILs for electrodepositing metals we decided to begin with plating Ni which is readily plated from both aqueous and IL media and there is guidance about the approaches to take (Gale, Gilbert et al. 1979; Pitner, Hussey et al. 1996). The next hurdle to surmount was the lack of information about the structure of the ions of Nb and Ta in the ILs and the type of metal deposits which could be obtained from them. We required a method which could provide in situ, both geometric and electronic structure information and we chose X-ray Absorption Spectroscopy, XAS. In this paper we report the structures that form when the chloride salts of Nb, Ta and Ni are dissolved in the room temperature ionic liquid 1-methyl-3-ethylimidazolium chloride (EMIC) and aluminum chloride (AlCl3). Further, we have studied the effects of the acid-base character of the ionic liquid on the structure of the ions in the IL solution. Since AlCl3 is a Lewis acid and EMIC is a Lewis base, they react forming a solution containing EMI+ ions and Cl− ions and their ratio determines the acidity of the solution.

EXPERIMENTAL

The preparation and purification of EMIC and AlCl3 were performed as described previously (Smith, Dworkin et al. 1989). All ionic liquid preparations were performed in a Vacuum Atmosphere drybox that was nitrogen filled, with oxygen and water concentrations below 1 ppm. The solutions were prepared by adding the anhydrous metal salts to the EMIC/AlCl3 ionic liquids with the appropriate mole fractions, with the AlCl3 fraction, N, determining acidity. By definition, a value of N < 0.5, is a basic solution and N > 0.5, is an acidic solution.
Approximately 25 mM of anhydrous Nb\textsubscript{2}Cl\textsubscript{10} or Ta\textsubscript{2}Cl\textsubscript{10} (Alfa Aesar, 99.999\%) were added to the basic and acidic AlCl\textsubscript{3}/EMIC ionic liquids. For the anhydrous NiCl\textsubscript{2}, the concentrations were 102 mM and 30 mM, respectively.

The EXAFS experiments were conducted on beamline X-11A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). All of the data were measured at room temperature with the storage ring operating at 2.8 MeV and beam currents in the range of 100 to 260 mA. The ionic liquid solutions were sealed in Kapton tubing (Small Parts, Inc.). The EXAFS data were collected at the K edges of Nb (18986 eV) and Ni (8333 eV) and the L\textsubscript{III} edge for Ta (9881 eV) in fluorescence mode using Si(311) crystals in the double crystal monochromator. Metal foils were used as the energy calibration references.

The data analysis are carried out using the XDAP code (Koningsberger, Mojet et al. 2000). The pre-edge background was removed by a linear extrapolation of the background to energies above the absorption edge and subtraction. A cubic spline polynomial was fit through the oscillations and subtracted from the spectra to remove the background absorption and isolate the EXAFS. The data were normalized to a per atom basis by dividing through by the step height of the absorption edge. By performing a Fourier transform (FT) on the EXAFS data, which is measured in k-space, one can obtain a radial structure function which is depicted in R-space. An individual coordination shell can be isolated from the EXAFS data by applying a forward FT followed by an inverse FT of one of the individual peaks found in the radial structure function (RSF) of the original data. The data analysis was conducted using both k\textsuperscript{1} and k\textsuperscript{3} weighted FTs. The ionic liquid systems studied have only low Z back scattering elements and the k\textsuperscript{1} weighting will emphasize the scattering from the low Z atoms (Koningsberger, Prins et al. 1988). The limits of the initial forward transforms were selected at the nodes of the \(\chi(k)\) function to reduce possible termination errors. The limits for the inverse transforms were chosen at the nodes in the imaginary part of the FT.

**RESULTS and DISCUSSIONS**

While the anhydrous NiCl\textsubscript{2} is an ionic salt, both anhydrous Nb\textsubscript{2}Cl\textsubscript{10} and Ta\textsubscript{2}Cl\textsubscript{10} salts are made up of two metal atoms in distorted octahedral configurations of six chlorides including two
bridging chlorides bonding the metal atoms together. The Nb_2Cl_{10} salt has two bridging chlorides at 2.56 Å bonding the two niobium atoms together at a distance of 3.95 Å. Each Nb has four additional chlorides, two equatorial chlorides at 2.25 Å and two axial chlorides at 2.30 Å (Zalkin and Sands 1958). The normalized k^3 weighted EXAFS spectra for the anhydrous niobium chloride powder and its radial structure function are shown in figures 1a and 1b, respectively. The niobium chloride was studied in acidic and basic melts of the AlCl_3/EMIC ionic liquid. The normalized k^1 weighted EXAFS spectra for the anhydrous niobium chloride dissolved in the N=0.60 ionic liquid and its FT are shown in figures 2a and 2b, respectively. The data show only

![Figure 1](image1.png)

**Figure 1.** (a) Normalized EXAFS spectrum for anhydrous Nb_2Cl_{10} powder. (b) The radial structure function (k^3, Δk=2.0 – 10.8 Å^{-1}) for the Nb_2Cl_{10} data shown in Fig. 1a.

![Figure 2](image2.png)

**Figure 2.** (a) The normalized EXAFS spectrum for Nb_2Cl_{10} in the N=0.60 acidic melt. (b) The radial structure function (k^1, Δk=2.4 – 11.8 Å^{-1}) for the Nb_2Cl_{10}/N=0.60 data shown in Fig. 2a.
one peak at low R values and no peaks at larger R distances as in figure 1b, indicating that there are no niobium-niobium interactions as in the powder sample and that the Nb₂Cl₁₀ dimer has broken apart similar to the reaction in the gas phase where two NbCl₅ molecules form trigonal bipyramid structures (Skinner and Sutton 1940; Konings and Booij 1994) It appears that a similar reaction also occurs in the acidic ionic liquid (Roeper, Pandya et al. 2009). These data were fit with a trigonal bipyramid model and the fits in k-space and R-phase are shown in figures 3a and 3b, respectively. The symmetric alignment of the imaginary and absolute data in the phase corrected R-space fit indicates that only chloride ions are associated with the niobium. Phase correction is necessary in order for the peaks to display at the correct distance.

![Figure 3](image-url)

Figure 3. (a) Isolated experimental (— ) and calculated (----) EXAFS functions for the first Nb-Cl shell for N=0.6 acidic melt (b) Imaginary parts and magnitudes of a phase corrected Fourier transform (k¹, Δk=4.3 – 11.0 Å⁻¹) performed on the EXAFS data shown in Fig 3a.

The normalized k¹ weighted EXAFS spectra for the anhydrous niobium chloride dissolved in the N=0.35 ionic liquid and its FT are shown in figures 4a and 4b, respectively. A large, low energy, shoulder is seen in the FT, indicating that the niobium is coordinated by ions at two different distances and possibly two different ions. A phase correction of the individual separated shells indicated that both ions are chloride ions but at two distances from the niobium central atom. The model that best fits these data is a square pyramid with a single axial chloride ion at a short distance and four chloride ions in a square plane at longer distances forming the base of the pyramid. The fits for k space and R space are shown in figures 5a and 5b, respectively. The phase corrected imaginary fits are not included because the 2 shell fit would not display the
necessary symmetry for chloride. The analyses are summarized in Table I. Note that the reported values for $\sigma^2$ are actually a $\Delta \sigma^2$, indicating the difference from the value used in the reference model.

Figure 4. (a) The normalized EXAFS spectrum for Nb$_2$Cl$_{10}$ in the N=0.35 basic melt. (b) The radial structure function ($k^1, \Delta k=2.1-12.2$ Å$^{-1}$) for the Nb$_2$Cl$_{10}$/N=0.35 data shown in Fig. 4a.

Figure 5. (a) Isolated experimental (...) and calculated (----) EXAFS functions for the two shell fit of Nb-Cl the shells in N=0.35 basic melt (b) Magnitude of the Fourier transform ($k^1, \Delta k = 3.0-11.2$ Å$^{-1}$) performed on the EXAFS data shown in Fig 5a.
Table I. EXAFS results for niobium chloride in acidic and basic solutions. N: coordination number, R: bond distance, $\Delta \sigma^2$: mean square relative displacement, $E_0$: inner potential correction, SD / SSR: standard deviation / sum of the square of residuals between experimental and calculated spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>$\Delta \sigma^2$ (Å²)</th>
<th>$\Delta E_0$ (eV)</th>
<th>SD / SSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>N = 0.60</td>
<td>Nb - Cl</td>
<td>5</td>
<td>2.31</td>
<td>-0.0010</td>
<td>-1.73</td>
<td>0.030 / 0.087</td>
</tr>
<tr>
<td>N = 0.35</td>
<td>1st Nb - Cl</td>
<td>1</td>
<td>1.91</td>
<td>-0.0005</td>
<td>-2.09</td>
<td>0.014 / 0.025</td>
</tr>
<tr>
<td></td>
<td>2nd Nb - Cl</td>
<td>4</td>
<td>2.41</td>
<td>0.0002</td>
<td>2.42</td>
<td>0.014 / 0.025</td>
</tr>
</tbody>
</table>

Ta$_2$Cl$_{10}$ breaks up into two TaCl$_5$ molecules in the acidic solution much the same as the Nb$_2$Cl$_{10}$ does. The TaCl$_5$ is not sufficiently basic to give up a chloride in the acidic solution. In the basic solution, the Ta$_2$Cl$_{10}$ also breaks up but forms a specie with an average coordination number of 7 chlorides, indicating that the TaCl$_5$ is a sufficiently strong Lewis acid to acquire additional chloride in the basic solution.

Figure 6. (a) The normalized EXAFS spectrum for Ta$_2$Cl$_{10}$ in the N=0.60 acidic solution. (b) normalized EXAFS spectrum for Ta$_2$Cl$_{10}$ in the N=0.43 basic solution.

The tantalum chloride was studied in acidic and basic solutions of the AlCl$_3$/EMIC ionic liquid. The normalized $k^3$ weighted EXAFS spectra for the anhydrous tantalum chloride dissolved in the acidic, N=0.60, and in the basic, N=0.43 solutions are shown in Figures 6a and 6b. These data
were fit with an octahedral model of tantalum with six chlorides and the fits in k-space and R-space are shown in Figures 7a and 7b, respectively for the acidic solution and in Figures 8a and 8b for the basic solution. The symmetric alignment of the imaginary and absolute data in the phase corrected R-space fit, Figure 7b, indicate that only chloride ions are associated with the tantalum atoms.

In the case of anhydrous NiCl₂, the coordination changes from tetrahedral in basic solution to octahedral in acidic solution. The NiCl₂ is also a stronger Lewis acid in that it can induce the aluminum chloride to share its chlorides in the strong acid solution (Roeper, Cheek et al. 2008; Roeper, Pandya et al. 2011) forming a structure with six near Cl⁻ ions and 8 further away Al ions which are sharing all the Cl⁻ ions surrounding the Ni²⁺. The results for NiCl₂ are summarized in Table III.

Figure 7. (a) Isolated experimental (——) and calculated (----) EXAFS functions for the Ta-Cl shell for N=0.60 acidic melt. (b) The imaginary part and magnitude of the phase corrected FT (k³, Δk=4.0 – 12.1 Å⁻¹) performed on the fit data shown in Figure 7(a).
Figure 8. (a) Isolated experimental (---) and calculated (-----) EXAFS functions for the Ta-Cl shell in N=0.43 basic melt. (b) The imaginary part and magnitude of the FT (k1, 12.2 Å) performed on the fit data shown in Figure 8(a).

**Table II.** EXAFS results for tantalum chloride in acidic and basic solutions. N: coordination number, R: bond distance, Δσ²: mean square relative displacement, E₀: inner potential correction, SD / SSR: standard deviation / sum of the square of residuals between experimental and calculated spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>Δσ² (Å²)</th>
<th>ΔE₀ (eV)</th>
<th>SD / SSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>N = 0.60</td>
<td>Ta - Cl</td>
<td>5</td>
<td>2.34</td>
<td>0.00002</td>
<td>-2.61</td>
<td>1.34 / 201.8</td>
</tr>
<tr>
<td>N = 0.43</td>
<td>Ta - Cl</td>
<td>7</td>
<td>2.35</td>
<td>0.0028</td>
<td>-7.58</td>
<td>0.91 / 89.0</td>
</tr>
</tbody>
</table>

**Table III.** EXAFS results for NiCl₂ in acidic and basic solutions. N: coordination number, R: bond distance, Δσ²: mean square relative displacement, E₀: inner potential correction, SD / SSR: standard deviation / sum of the square of residuals between experimental and calculated spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>Δσ² (Å²)</th>
<th>ΔE₀ (eV)</th>
<th>SD / SSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>N=0.43</td>
<td>Ni - Cl</td>
<td>4</td>
<td>2.28</td>
<td>-0.0027</td>
<td>-1.84</td>
<td>0.032 / 0.134</td>
</tr>
<tr>
<td>N=0.54</td>
<td>Ni - Cl</td>
<td>6</td>
<td>2.37</td>
<td>0.0046</td>
<td>0.89</td>
<td>0.031 / 0.080</td>
</tr>
<tr>
<td>N=0.60</td>
<td>Ni - Cl</td>
<td>6</td>
<td>2.41</td>
<td>0.0016</td>
<td>2.03</td>
<td>0.018 / 0.033</td>
</tr>
<tr>
<td></td>
<td>Ni - Al</td>
<td>8</td>
<td>3.25</td>
<td>0.0090</td>
<td>-0.40</td>
<td>0.013 / 0.017</td>
</tr>
</tbody>
</table>
CONCLUSIONS

The coordination environment of several transition metal chlorides in basic and acidic ionic liquids has been revealed using EXAFS analysis. The EXAFS data for Nb₂Cl₁₀ and Ta₂Cl₁₀ in the acidic IL indicate that both dimers come apart to form trigonal bipyramidal structures, but form more complex structures in the basic IL. The data for NiCl₂ indicates that it has the simpler tetrahedral structure in the basic IL but has a more complex structural arrangement with the aluminum chloride in the acidic melt. This may be the reason that nickel is more readily electrodeposited from the acidic IL than the niobium or tantalum.

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REFERENCES


