Electrochemical Deposition of Molybdenum and Tungsten from Trinuclear Metal Clusters \((M_3O_2(OAC)_6(H_2O)_3(CF_3SO_3)_2)\) in 1-Ethyl-3-Methylimidazolium tetrafluoroborate ionic

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ELECTROCHEMICAL DEPOSITION OF MOLYBDENUM AND TUNGSTEN FROM TRINUCLEAR METAL CLUSTERS 
(M₃O₂(OAC)₆(H₂O)₃(CF₃SO₃)₂) IN 1-ETHYL-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE IONIC LIQUID

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY CHARLES JOSEPH WOODS ENTITLED Electrochemical Deposition of Molybdenum and Tungsten from Trinuclear Metal Clusters (M₃O₂(OAc)₆(H₂O)₃(CF₃SO₃)₂) in 1-Ethyl-3-Methylimidazolium Tetrafluoroborate Ionic Liquid BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

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Electrochemical properties of \(\text{Mo}_2\text{WO}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2\) and \(\text{W}_3\text{O}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2\) clusters in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF\(_4\)) ionic liquid was investigated. Cyclic voltammograms using a platinum electrode indicated that deposition of metal had occurred. Constant potential electrolysis of \(\text{Mo}_2\text{WO}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2\) at -1.9 V using a platinum foil electrode was performed. Atomic force microscopy (AFM) confirmed that deposition had occurred.
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I. INTRODUCTION

**Molten Salts**

Molten salts, or “fused salts”\(^1\), are inorganic salts at a temperature above their melting point. For example, sodium chloride (NaCl), melts at approximately 800ºC (1474ºF) \(^1\). Once in their liquid form, inorganic salts can be used in a variety of ways. Molten salts are commonly used in the electrolytic production of various metals such as aluminum and uranium. As in most cases, there are both benefits and disadvantages with using molten salts. They possess good chemical, conductive, and heat transfer properties, they are relatively stable at high temperatures, and they have a very low vapor pressure.\(^2\) Some of their disadvantages include their tendencies to be hydroscopic, corrosive, and hard to characterize as well as extra safety precautions should be taken due to their high melting points.

**Ionic Liquids**

Ionic liquids are similar to molten salts except that they are liquid at room temperature and more commonly contain strong ion-ion interactions. Ionic liquids include a bulkier organic cation and a smaller inorganic anion.\(^7\)
Substituting the cations and anions or altering the chain length can vary the liquid’s properties. More significantly, choosing the correct anion is a crucial part in determining the best ionic liquid for a given task. Although anions such as BF$_4^-$ and CF$_3$SO$_4^-$ are thermally stable and both air and water insensitive, they produce different ionic liquids that may have different properties. However, substituting the cation portion plays a role in affecting the ionic liquid’s melting point and electrochemical window. Some commonly used cations are a) Alkylsulfonium, b) alkylphosphonium, c) alkylammonium, d) N,N’-alkylimidazolium, and e) N-alkylpyridinium.

\[
\text{a) } [S_{X}R_{3-X}]^{+} \quad \text{b) } [P_{X}R_{4-X}]^{+} \quad \text{c) } [N_{X}R_{4-X}]^{+}
\]

![Chemical structures of cations](image)

**Figure 1.** Five Commonly Used Cations in Ionic Liquid Synthesis.
Due to their strong ionic interactions, ionic liquids have characteristic properties. Some of these properties are increased thermal stability, stability in air and water, and large electrochemical windows. Ionic liquids also have advantages over many organic solvents such as low vapor pressure, high conductivity, higher density, and high potential window. Other advantages include higher yields, more cost efficient, and environmental friendly alternatives for volatile organic compounds (VOCs). Ionic liquids are used in various products and processes including batteries and metal electrodeposition.

Presently, ionic liquids are used as environmentally friendly solvents for electro and organic synthesis. They are commonly referred to as “green solvents” in organic and organometallic chemistry because of their environmentally friendly properties.

1,3-Dialkylimidazolium Salts

The 1,3-dialkylimidazolium cation is a major one used today to form ionic liquids.
Figure 2. N,N-dialkylimidazolium Cation.

The R is most commonly a methyl group while R’ can be changed.\(^\text{15}\)

The catonic part may be:

\[
\begin{align*}
R' &= \text{Methyl} \quad \text{MMIm}^+ \quad \text{C}_5\text{H}_9\text{N}_2^+ \\
&= \text{Ethyl} \quad \text{EMIm}^+ \quad \text{C}_6\text{H}_{11}\text{N}_2^+ \\
&= \text{Propyl} \quad \text{PrMIm}^+ \quad \text{C}_7\text{H}_{13}\text{N}_2^+ \\
&= \text{Isopropyl} \quad \text{iPrMIm}^+ \quad \text{C}_7\text{H}_{13}\text{N}_2^+ 
\end{align*}
\]
The anionic part may be:

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<th>Tetrafluoroborate</th>
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<tr>
<th>Bis((trifluoromethyl)sulfonyl)imide</th>
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<td><img src="image4" alt="Bis((trifluoromethyl)sulfonyl)imide" /></td>
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Different combinations of cations, anions, and alkyl chain length affect the chemical and physical properties of an ionic liquid. The anion is indirectly involved in the viscosity and melting point due to its hydrogen bonding whereas choosing the right cation for cation-anion attraction influences the driving force of the ionic liquid reactions. Altering the alkyl
chain length can affect the crystallization and hydrophobic effects of ionic liquids.

![Chemical structure](image)

Figure 3. 1-Ethyl-3-Methylimidazolium Cation and Tetrafluoroborate Anion.

**Metal Cluster Compounds**

Metal clusters are compounds containing at least two metal ions bonded together by direct metal-metal bonds. Transition metals on the second and third rows of the periodic table very readily form metal cluster compounds. Their clusters can be classified as either early or late transitional metal clusters. Early transitional metal clusters contain electron poor metals, such as molybdenum, tungsten, tantalum, or niobium, in their relatively high oxidation state. The ligands for these clusters, such as O\(^2\), Cl\(^-\), Br\(^-\), and I\(^-\), donate their \(\pi\)-electrons to the metal atom. In order to
stabilize the metal cluster, high oxidation states of metal ions are desired. This in turn can optimize the metal-metal bonding effects. Late transitional metal clusters are formed using the lower oxidation state of a metal such as rhodium or iridium, which tend to be more electron rich. The ligands for these clusters, such as carbonyls, carbon monoxide, and phosphine, are electron accepting. The first transition metal cluster, \((\text{Ta}_6\text{Cl}_{12})\text{Cl}_2\cdot8\text{H}_2\text{O}\), was discovered and characterized by Linus Pauling in 1950.\(^{27}\) The structure of \((\text{Ta}_6\text{Cl}_{12})\text{Cl}_2\cdot8\text{H}_2\text{O}\) was found by x-ray diffraction in EtOH solution. Six tantalum ions form an octahedron and twelve Cl\(^-\) ions each bridge two Ta atoms. The formal oxidation state of Ta was +2.33. Therefore, there are 16 electrons forming the Ta-Ta bond giving a Ta-Ta bond order of \(16/24 = 0.666\).

Figure 4. \(\text{Ta}_6\text{Cl}_{12}^{2+}\) hexanuclear cluster.\(^{27}\)
Main Structural Types of Early Transitional Metal Clusters

Three of the most common structural types of early transition metal clusters include binuclear, trinuclear and hexanuclear clusters.

Binuclear Metal Clusters

Binuclear metal clusters contain multiply bonded M-M dimers with bond order of 1 up to 4. The common examples include Re$_2$X$_8^{2-}$ and binuclear metal carboxylates M$_2$(O$_2$CR)$_4$ (M = Cr, Mo, W, Re, Ru). The most interesting features in Re$_2$X$_8^{2-}$ and M$_2$(O$_2$CR)$_4$ are very short M-M distance of 2.24 Å (Re$_2$X$_8^{2-}$) and 2.0 Å in Mo$_2$(O$_2$CR)$_4$, which are shorter than M-M distances in metals. The second characteristic is the eclipsed configuration of ligand donor atoms as shown in Figure 5.

![Figure 5. The structure of the octachlorodirhenate (III) ion, Re$_2$Cl$_8^{2-}$.](image-url)
The M-M bonding between Re-Re atoms was described by F.A. Cotton and consists of a σ bond (using $d_z^2$ orbitals) and two π bonds (formed by overlap of $d_{xz}$ and $d_{y^2}$ orbitals) shown in Figure 6.
The fourth metal-metal bond is formed by the overlap of the $d_{xy}$ orbital (Figure 6c). This sideways overlap results in the formation of delta bond ($\delta$). This $\delta$ orbital overlap can occur only if the Cl\(^{-}\) atoms are in an eclipsed configuration. There are 4 d electrons on each Re atoms forming 4 Re-Re bonds. The structure of M\(_2\)(O\(_2\)CR)\(_4\) (M = Mo, W, Cr) is shown in Figure 7.
The formal oxidation state of Mo in $\text{Mo}_2(\text{O}_2\text{CR})_4$ is 2+. Therefore, 4d electrons of each Mo overlap forming a quadruple Mo-Mo bond ($\sigma$, $2\pi$, $\delta$). Quadruply bonded Mo dimers can be successfully oxidized by 1e$^-$ to form dimers with a bond order of 3.5.

$$\text{Mo}_2(\text{O}_2\text{CR})_4 - e^- \rightarrow \text{Mo}_2(\text{O}_2\text{CR})_4^+ \rightarrow e^- \rightarrow \text{Mo}_2(\text{O}_2\text{CR})_4^{2+}$$

Mixed metal quadruple bonded dimers $\text{MoW}(\text{O}_2\text{CCH}_4)_3$ have been also prepared.
Trinuclear Metal Clusters

There are three types of trinuclear clusters:

1. Clusters with no capping ligands, $M_3X_6$, Formula = $[M_3X_6(C_6Me_6)_3]^{n+}$, where $M =$ Ti, Nb, or Ta and $X =$ Cl or Br.

![Figure 8. Structure of trinuclear metal cluster Type #1 with no capping ligands.](image)

2. Clusters with one capping ligand, $M_3X_{13}$, Formula = $[M_3(\mu_3-X)(\mu-Y)_3L_9]$, where $M =$ Mo, W, Nb, or Ti; $X$ (capping ligand) = S$^{2-}$, O$^{2-}$, Cl$^{-}$, Br$^{-}$, I$^{-}$, or OCH$_2$CMe$_3$; $Y$ (bridging ligand) = S$^{2-}$, O$^{2-}$, Cl$^{-}$, Br$^{-}$, I$^{-}$; $L$ (terminal ligands) = Cl$^{-}$, Br$^{-}$, I$^{-}$, H$_2$O, CN$^{-}$, OEt$^{-}$, or O$_2$CCMe$_3$.
3. Clusters with two capping ligands, $M_3X_{17}$, Formula =

$[M_3(\mu_3-X)(\mu-O_2Y)_6L_3]$, where $M = W$ or Mo; $X = \text{OEt}^-$ or $\text{O}^{2-}$; $Y$ (bidentate ligands) = tBuCO$_2$, MeCO$_2$, or EtCO$_2$; $L$ (monodentate ligands) = H$_2$O, tBuCO$_2$, or MeCO$_2$.

Figure 9. Structure of trinuclear metal cluster Type #2 with one capping ligand.
Figure 10. Structure of trinuclear metal cluster Type #3 with two capping ligands.

Tungsten, molybdenum, and other early transition metals in their lower oxidation states have a triangular $M_3$ unit and frequently have bond orders of $2/3$ to $1$. Tungsten and molybdenum can usually be classified as having structure type #3, which has a core symmetry of $D_{3h}^{16}$. Examples of a cluster having the #3 structure type would be $W_3O_2(O_2CCH_3)_6(H_2O)_3^{2+}$ and $Mo_3O_2(O_2CCH_3)_6(H_2O)_3^{2+}$. The formal oxidation state of the metal atoms is $4+$ ($2+ = 3x - 4 - 6; 3x = 12; x = 12/3 = 4+$). Each metal atom contributes two electrons to form three single bonds between the metal atoms giving the $M - M$ bond order of one. The metal-metal bonding in this cluster is a result of the overlap of $4\ dz^2$ and $4\ dx$ metal orbitals. Combination of $3\ dz^2$
orbitals gives a MO orbital of $a_1$ symmetry and combination of 3 $d_{xy}$ and 3 $d^2y$ orbitals gives a MO of $1e'$ symmetry.

Figure 11. Overlap of 4 $dz^2$ and 4 $dx$ metal orbitals in a $M_3O_2(OR)_6(L)_3$ cluster.

Mixed – metal isostructural trinuclear clusters of Mo and W such as $Mo_2W(OAc)_6(H_2O)_3^{2+}$ and $MoW_2(OAc)_6(H_2O)_3^{2+}$ have been previously prepared. They were synthesized by reactions between quadruple bonded dimers $Mo_2(OAc)_4$ or $MoW(OAc)_4$ with $MoO_4^{2-}$ or $WO_4^{2-}$.

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Hexanuclear Metal Clusters

Hexanuclear clusters contain six metal atoms and are created by forming either single bonds to the other metal atoms or multiple metal–metal bonds. These metal clusters form two different types:

1. The metal atoms form an octahedral configuration and eight ligands are arranged so that each bridge three metal atoms together.

2. The second type is similar to #1 except that there are 12 ligands each bridging two metal atoms.

Figure 12. Examples of Hexanuclear metal clusters.
**Electrochemical Method**

Electrochemical methods are techniques that measure the redox properties of an analyte in an electrochemical cell. There are three major types of electrochemical methods: coulometry, potentiometry, and voltammetry. Coulometry is the measurement of electric charge during electrolysis, potentiometry is the measurement of potential as a function of concentration of analyte, and voltammetry is the correlation between applied potential and current.

**Cyclic Voltammetry**

Cyclic voltammetry (CV) is a simple electrochemical technique that involves cycling the potential of an electrode between two values and measuring the resulting response in current. This technique can be used to study redox properties of various inorganic and organic molecules. The electrochemical cell utilizes a three electrode system consisting of the auxiliary electrode, working electrode, and reference electrode. Cyclic voltammetry can provide rapid location of redox potentials and the kinetics of heterogeneous electron-transfer reactions. Furthermore, it offers convenient analysis of the influence of media on the redox process.
Figure 13. Diagram of the three electrode electrochemical cell used for cyclic voltammetry.

The current is measured between the counter electrode and the reference electrode as a function of applied potential. During the reduction sweep, or forward scan, the initial potential is more positive than the final potential and the current is due to the reduction of the species. During the reverse scan of the cycle, anodic current is due to the re-oxidation of the reduced species. Figure 14 shows the time potential profile in a cyclic voltammogram.
Figure 14. Cyclic Voltammetric triangular potential cycle.

Figure 15. A Cyclic Voltammogram of Fe(CN)$_6^{3-}$. 
There are four parameters that a cyclic voltammogram can provide. The anodic peak current, $I_{pa}$, the cathodic peak current, $I_{pc}$, the anodic peak potential, $E_{pa}$, and the cathodic peak potential, $E_{pc}$. Using these four values, the number of transferred electrons, $n$, the standard reduction potential, $E^\circ$, and the heterogeneous rate constant, $K_n$, can be determined.

$$E_{1/2} = E_{pc} + 1.11 \ (RT/nF)$$  \hspace{1cm} (1)

The current-potential curve for planar electrodes is given by the Randle-Sevcik equation:
\[ I_p = \left( nF \right)^{3/2} A (\nu D)^{1/2} C \Psi / [RT]^{1/2} \] (2)

- \( A \) = working electrode area (cm²)
- \( C \) = analyte concentration (m/cm³)
- \( D \) = diffusion coefficient (cm²/s)
- \( \nu \) = potential scan rate (V/s)

The \( \Psi \) function reaches the maximum value of 0.416 when \( E - E_{1/2} \) is -28.5 mV. The rate constant determines if the reaction is electrochemically reversible, irreversible, or quasi-reversible, which is displayed in Figure 17.

If there is a slow electron exchange during the redox reaction, then the system is irreversible i.e. the standard rate constant \( k^o \) is very small.

The peak potential, \( E_{pa} - E_{pc} \), separation for one electron in a reversible system should be 0.0592 V. The standard reduction potential for this reaction can be calculated by equation (3):

\[ E^\circ = (E_{pa} + E_{pc})/2 \] (3)

\[ \Delta E = E_{pa} - E_{pc} = 0.0592/n \] (4)
In order to determine if a system is irreversible from a cyclic voltammogram, the current from the reverse sweep will not be displayed. The peak potential separation is more than 59.2 Volts in a quasi-reversible system and increases with increasing scan rate.

Figure 17. Cyclic Voltammograms of: A. Reversible and B. Quasi-reversible processes.

**Electrodeposition of Metals**

The electrodeposition of chloroaluminate melts was first performed using AlCl₃-based melts. Most research on metal deposition has been done in chloroaluminate melts. However, there are several disadvantages when
using these molten salts. Although they can generally dissolve a variety of metal salts, these melts not only are very air- and water- sensitive, but also corrosive. As a result, several research groups have tried to synthesize different molten salts in which the disadvantages of AlCl$_3$ – based salts are absent.

There are currently three types of metal salts. The first group contains chloroaluminate anions and the second and third generations of molten salts are air- and water- stable melts. One of the main advantages the second and third generations of molten salts have over the first generation of molten salts is that they can be prepared and stored absent of an inert atmosphere. For example, molten salts based on trifluoromethaneulfonate anion (CF$_3$SO$_3^-$) have been given extraordinary attention because in addition to their air- and water- stability, they have large electrochemical windows. Large electrochemical windows have enabled the use of ionic liquids in the electrodeposition of metals, a feature molten salts have over aqueous solutions at moderate temperatures. The following describes the deposition of metals, including chromium, palladium, platinum, copper, and silver.
Chromium

By mixing choline chloride (C₅H₁₄ClNO) and chromium(III) chloride hexahydrate, a dark green, viscous liquid, which has similar physical properties as an ionic liquid, has been synthesized. Chromium can be electrodeposited from this liquid to yield a seamless deposition of the metal. Although this chromium electrodeposition process may provide a more environmentally friendly method compared to the acid-based baths, more research is still needed to be able to compete with the shining chromium deposits involved in the Cr(VI)- or Cr(III)- based aqueous galvanic technique.

Palladium

Palladium has a high catalytic activity for many chemical reactions. However, due to its ability to absorb hydrogen, only fragile deposits can be obtained in aqueous solutions. On the other hand, one of the advantages of using ionic liquids is that hydrogen evolution is absent. Sun et al. obtained compact alloy deposits with the Pd content increasing as the mole fraction of Pd increased in the plating bath⁵².
**Platinum**

Like palladium, platinum crystals are also used as catalysts in several chemical reactions. There is also no hydrogen evolution observed in the electrodeposition of platinum when using ionic liquids. This is important because the quality of platinum deposits can be affected otherwise. Pt nanocrystals were reported as shiny, dense, and smaller than 100 nm.\(^\text{22}\)

**Copper**

With several excellent properties, copper has gained extra attention particularly by the semiconductor industry. The electrochemical deposition of Cu has been further investigated in order to solve the tantalum diffusion barrier problem. At this barrier, the deposition of copper has to compete with the formation of tantalum oxide. Therefore, other ways to carry out the electrodeposition of copper in ionic liquids have been investigated. For example, Sun *et al.* showed that Cu can be electrodeposited in a basic chloride containing 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMImBF\(_4\)). The electrodeposition of
nanocrystalline copper not only can serve as an important catalyst, but also has superior mechanical and electrical properties compared to that of microcrystalline copper.

Silver

Although the electrodeposition of silver from chloroaluminate melts has been investigated, Katayama et al. reported that room temperature ionic liquids could serve as suitable substitutes for electroplating baths for silver. Room temperature ionic liquids are advantageous because they prevent the contamination of aluminum while performing the electrodeposition of silver. Silver can be deposited with relative ease when using second and third generation ionic liquids.
II. EXPERIMENTAL

Materials

1-Methylimidazole (99%) was purchased from Aldrich Chemical Company Inc. It was purified by distillation at 100°C under vacuo (30 mmHg). Ethyl chloride (99.7%) and Sodium Tetraflouroborate (98%) were purchased from Aldrich Chemical Company Inc. The solvents were either ACS reagent grade or ACS certified and were used as received. Acetonitrile (99.9%) was purchased from Alfa Aesar and used as received. Anhydrous ethyl ether was purchase from Fisher Chemicals. Dichloromethan (99%) was purchased from EM Science, ACS grade, and was used as received.

Instrumentation

The water content of the ionic liquid was determined using a Denver Instrument Coulometric Karl Fisher Titrator that was interfaced with a Model 260 titrator controller. A stainless steel syringe was used to inject approximately 100 microliters of ionic liquid into the titrator. The syringe was washed in acetonitrile and dried in an oven set at approximately 60°C to 80°C between uses.
Cyclic Voltammetry experiments were performed using an EG&G Princeton Applied Research C (PARC) 173 Potentiostat/Galvanostat System with a PAR 175 Universal Programmer interfaced with a Houston Omnigraphic XY 2000 recorder or Maclab 4 analog to digital converter. The cyclic voltammograms were obtained by utilizing a glassy carbon or platinum disc working electrode, a Ag/AgCl reference electrode, and a platinum auxiliary electrode. The glassy carbon and platinum disc electrodes (1mm²) were obtained from Cypress Systems Inc. The cell volume ranged from 0.5mL to 1mL. An example of an electrochemical cell is shown in Figure 18.

![Electrochemical cell](image)

Figure 18: Electrochemical cell used for CV measurements.
Absorption spectra were obtained by an Ocean Optics Spectra Suite USB 4000 spectrometer using an Ocean Optics LS-1 tungsten halogen lamp.

**Preparation of 1-Ethyl-3-Methylimidazolium Chloride**

1-Ethyl-3-Methylimidazolium Chloride (EMICl) was prepared using a modified literature method, from 1-Methylimidazole and ethyl chloride. An ACE glass reinforced pressure flask was placed inside a nitrogen filled I2R glove bag. The flask was cooled in a liquid nitrogen/ethanol bath to allow gaseous ethyl chloride to condense by cooling it down to approximately -40°C until 89.06g were obtained. Distilled 1-Methylimidazole (90.43g) was added to the flask and a Teflon screw cap was used to close the flask. The reaction flask was then placed in an oil bath to maintain a constant temperature of about 35°C and allowed to stir for 10 to 14 days. Reaction progress was monitored by observing the amount of immiscible layer of EMICl at the bottom of the flask. Once complete, the flask was placed in a freezer overnight and white crystals of EMICl were formed. The remaining liquid was decanted and the solid EMICl was dissolved in a minimum amount of acetonitrile. The addition of ethyl ether caused the EMICl to precipitate and after cooling in a refrigerator overnight, large white crystals
then formed. The crystals were filtered under nitrogen using a Schlenk filter apparatus and dried under a vacuum.

**Preparation of 1-Ethyl-3-Methylimidazolium Tetrafluoroborate**

1-Ethyl-3-Methylimidazolium Chloride and sodium tetrafluoroborate (NaBF₄) were used to form 1-Ethyl-3-Methylimidazolium Tetrafluoroborate (EMIBF₄). 89.12g (0.6078mol) of EMICl and 70.94g (0.6461mol) of NaBF₄ were each dissolved in 300 mL of distilled water. The two mixtures were then combined and allowed to stir overnight. The white NaCl precipitate was filtered from the solution and the solvent was removed by using a rotary evaporator. The filtering and evaporating process was continued until the remaining liquid was pure EMIBF₄ without Cl⁻. The last traces of Cl⁻ were recovered by potentiometric titration with AgBF₄.

**Preparation of Mo₂WO₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂**

The two trinuclear metal clusters Mo₂WO₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂ and W₃O₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂ were previously prepared¹¹. Sodium tungstate (Na₂WO₄) was combined with a molybdenum dimer (Mo₂(O₂CCH₃)₄) using a molar ratio of
approximately 3:1, respectively. This was accomplished by first preparing a
deaerated solution (N₂ for 20 min.) of 75 ml glacial acetic acid, 7 ml of
acetic anhydride, and 1 ml of triethylamine in a 200 ml schlenk flask. Then,
3.923 g (13.35 mmol) of ground sodium tungstate via mortar and pestle was
added. These reagents were stirred and refluxed using a condenser until the
salt was dissolved, taking approximately 25 minutes. After that, 1.701 g
(3.974 mmol) of the molybdenum dimer (Mo₂(OAc)₄) was added to the
mixture, which was refluxed and stirred for 9 days. Once the mixture cooled
to room temperature, 100 ml of distilled water was added. This solution was
poured on an acidified DOWEX 50WX2-200 (H) cation exchange resin
column. The column was rinsed with water and then eluted with 1.0 M
CF₃SO₃H. After cooling the eluent, crystals of
Mo₂WO₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂ were obtained.
III. RESULTS AND DISCUSSION

Synthesis and Electrochemistry of EMIBF$_4$

Synthesis of EMIBF$_4$ was done in a two step process. First, n-Methylimidazole was reacted with ethyl chloride to give 1-methyl-3-ethyl imidazolium chloride.

![Chemical structure](image)

Figure 19. Ethylation of n-Methylimidazole

The second step includes substitution of Cl$^-$ anions with BF$_4^-$ anions. This was done via metathesis reaction in water using sodium tetrafluoroborate (NaBF$_4$).
NaCl by-product was removed by filtration and excess Cl\(^-\) anions were removed by potentiometric titration with AgBF\(_4\) until the equivalence potential was obtained. Figure 21 shows the potentiometric equivalence point determined by titration of Cl\(^-\) with AgBF\(_4\). It was determined to be approximately at 255 mV. After the equivalence potential was experimentally determined using a particular set of electrodes, the aqueous solution of ionic liquid which contained Cl\(^-\) impurities was titrated until the previously determined equivalence potential was obtained. Figure 22 shows a cyclic voltammogram of pure EMIBF\(_4\), which should have a potential window of 4.2V. The voltammogram does not display an oxidation peak at 1.0 V due to the oxidation of Cl\(^-\).
Figure 21. Potentiometric Equivalence Point determined by the titration of AgBF$_4$ and Cl$^-$ anions with AgBF$_4$. 

<table>
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<tr>
<th>Drops of AgNO3</th>
<th>Potential (mV)</th>
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<tr>
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Once excess water was evaporated by drying EMIBF$_4$ in a vacuum at about 41°C for several days, the amount of remaining moisture was determined via Karl-Fisher coulometric titration. The infrared spectrum of dry EMIBF$_4$ is shown in Figure 23. Only relatively small H$_2$O stretching bands are observed at $\sim$3600 cm$^{-1}$. These two bands correspond to antisymmetric and symmetric stretching of H$_2$O. If a larger amount of H$_2$O is present (> 300 ppm), a broad band at $\sim$3400 cm$^{-1}$ is observed, a characteristic of the presence of hydrogen bonding.
Electrochemistry of Trinuclear Metal Clusters in Ionic Liquids

Electrochemical properties of $W_3O_2(O_2CCH_3)_6(H_2O)_3(CF_3SO_3)_2$ and $Mo_2WO_2(OAc)_6(H_2O)_3(CF_3SO_3)_2$ trinuclear clusters in ionic liquids were compared to their electrochemical properties in MeOH. The metal clusters, $W_3O_2(O_2CCH_3)_6(H_2O)_3(CF_3SO_3)_2$ and $Mo_2WO_2(OAc)_6(H_2O)_3(CF_3SO_3)_2$, readily dissolve in MeOH, however, they had to be heated up to 60°C for several days in a closed vial to dissolve in EMIBF$_4$. Comparison of
electronic spectra of \( \text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2 \) cluster obtained in MeOH and in EMIBF₄ are shown in Figures 26-28. Figure 25 shows the electronic spectrum of pure EMIBF₄. Similarly, the electronic spectra of tungsten trimers, \( \text{W}_3\text{O}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2 \), obtained in MeOH and EMIBF₄ ionic liquid are identical confirming that the trinuclear structure of the clusters did not change by dissolving them in ionic liquid.

![Image of molecular structures]

Figure 24. Structures of \( \text{W}_3\text{O}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2 \) and \( \text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2 \).
Figure 25. Electronic Absorption Spectrum of EMIBF$_4$.

Figure 26. Electronic Absorption Spectrum of Mo$_2$WO$_2$(OAc)$_6$(H$_2$O)$_3$(CF$_3$SO$_3$)$_2$ dissolved in MeOH.
Figure 27. Electronic Absorption Spectrum of Mo$_2$WO$_2$(OAc)$_6$(H$_2$O)$_3$(CF$_3$SO$_3$)$_2$ dissolved in EMIBF$_4$.

Figure 28. Comparison of Electronic Absorption Spectra of Mo$_2$WO$_2$(OAc)$_6$(H$_2$O)$_3$(CF$_3$SO$_3$)$_2$ dissolved in MeOH (A) and EMIBF$_4$ (B).
Electrochemistry of $\text{Mo}_2\text{WO}_2\text{(OAc)}_6\text{(H}_2\text{O)}_3\text{(CF}_3\text{SO}_3)_2$

Cyclic voltammograms of $\text{Mo}_2\text{WO}_2\text{(OAc)}_6\text{(H}_2\text{O)}_3\text{(CF}_3\text{SO}_3)_2$ dissolved in EMIBF$_4$ ionic liquid using a platinum electrode and a glassy carbon electrode are shown in Figure 29. The voltammogram of $\text{Mo}_2\text{WO}_2\text{(OAc)}_6\text{(H}_2\text{O)}_3\text{(CF}_3\text{SO}_3)_2$ on Pt electrode in Figure 29A was initiated at 0.5 V and scanned in negative direction and reversed at -1.3 V. The voltammogram displays a reduction peak at -0.8 V and an oxidation peak at $E = 1.1$ V. The reduction peak at -0.8 V shows only a small amount of current on the reverse sweep indicating that a chemical step follows the initial electrochemical step (EC process). The oxidation peak at $E = 1.1$ V does not show re-reduction current on the reverse scan indicating that the oxidized product is not stable on the CV scale of the experiment. Both of these peaks are of the same magnitude. They could be assigned to a one-electron process.
Figure 29. Cyclic voltammograms of $\left[\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3\right]^{2+}$ dissolved in EMIBF$_4$ using a platinum electrode (A) and a glassy carbon electrode (B).

$$E_{p,c} = -0.8 \text{ V}$$

$$[\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3]^{2+} + \text{e}^- \rightarrow$$

$$[\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3]^+ + \text{C} \rightarrow \text{Product}$$
\[ E_{p,a} = 1.1 \text{ V} \]

\[ [\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3]^{2+} - \text{e}^{-} \rightarrow [\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3]^{3+} + \text{C} \rightarrow \text{Product} \]

However, the reduction and oxidation products are not stable on the time scale of the CV experiment and they undergo further chemistry. The cyclic voltammogram obtained using a GC electrode is different than the CV obtained on a Pt electrode and shows only one irreversible reduction peak at \( E = -1.4 \text{ V} \). When using a Pt electrode, if the negative sweep is continued more negative, then at \( E = -1.3 \text{ V} \) a large cathodic current is obtained which is due to the reduction of \( \text{Mo}_2\text{W} \) trimer to metal which is deposited on the electrode. A cyclic voltammogram of \( \text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2 \) trimer in EMIBF\(_4\) scanned in the negative direction and reversed at \( E = -1.9 \text{ V} \) is shown in Figure 30.
The voltammogram displays a reduction peak at ~E = -1.0 V and a large cathodic current at E = -1.8 V. When the potential is held for several seconds at -1.9 V and then reversed, a large anodic peak is observed at E = -0.3 V. This anodic peak becomes larger if the reduction potential is held longer before reversal. This is a typical CV obtained when the reduction and deposition of metal occurs. We propose that at a potential of E = -1.9 V, a
complete reduction of $\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2$ cluster to metal using 12 electrons takes place.

$$[\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3]^{2+} + 12\text{e}^- \rightarrow \text{Mo}_2\text{W}$$

This relatively easy deposition of metal on the Pt electrode could be explained by bonding of the metal atom of $\text{Mo}_2\text{W}$ cluster unit to Pt. It is possible that the $\text{M}_3$ cluster in ionic liquid releases one $\text{H}_2\text{O}$ molecule in the $[\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3]^{2+}$ cluster resulting in emptying one equatorial coordination site of $\text{M}_3$ clusters open to bind to the Pt electron.

Figure 31. Proposed bonding between the $\text{M}_3$ cluster and platinum electrode.
This allows an easy transfer of electrons to the cluster and formation of $M^0$ deposition. To prove that a deposition of metal occurs, a constant potential reduction on a large Pt electrode was performed. A two compartment electrochemical cell as shown in Figure 32 was used.

Figure 32. Two compartment electrochemical cell used for electrodeposition of metal from EMIBF$_4$ ionic liquid.$^{24}$
A Pt foil (~25 mm²) working electrode and Ag/AgCl reference electrode were placed in the cathodic compartment. The auxiliary Pt electrode was placed in the anodic compartment. The solution of \([\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3]^{2+}\) was electrolyzed at -1.9 V for ~16 hours. Inspection of the Pt electrode under the microscope indicates that a deposition has occurred. Atomic force microscopy images of the Pt electrode show that the deposition of Mo and W has occurred. Figures 33 – 36 show the AFM images obtained of Pt electrode after reduction of \(\text{Mo}_2\text{W}\) trimer.
Figure 33. Atomic force microscopy image of Mo$_2$W deposited by electrochemical reduction of [Mo$_2$WO$_2$(OAc)$_6$(H$_2$O)$_3$]$^{2+}$ Pt electrode (resolution x=0-50 μm).
Figure 34. Atomic force microscopy image of Mo$_2$W deposited by electrochemical reduction of [Mo$_2$WO$_2$(OAc)$_6$(H$_2$O)$_3$]$^{2+}$ Pt electrode (resolution x = 0-20 μm).
Figure 35. Atomic force microscopy image of Mo$_2$W deposited by electrochemical reduction of [Mo$_2$WO$_2$(OAc)$_6$(H$_2$O)$_3$]$^{2+}$ Pt electrode (resolution x = 0-10 μm).
Figure 36. AFM profile measurements of Mo$_2$W electrodeposited on Pt electrode. $^{25}$
**Electrochemistry of W₃O₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂**

Electronic spectrum of W₃O₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂ dissolved in MeOH is shown in Figure 38. It shows two absorption maxima at 360 and 450 nm. The spectrum of W₃O₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂ dissolved in EMIBF₄ ionic liquid is very similar to the spectrum obtained in MeOH. The comparisons of W₃O₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂ spectra obtained in MeOH and EMIBF₄ ionic liquid are shown in Figure 38.

![Figure 37. Electronic Absorption Spectrum of W₃O₂(O₂CCH₃)₆(H₂O)₃(CF₃SO₃)₂ dissolved in EMIBF₄.](image)
Figure 38. Comparison of Electronic Absorption Spectra of $\text{W}_3\text{O}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2$ dissolved in EMIBF$_4$ (A) and MeOH (B).
Figure 39. Cyclic Voltammogram of $\text{W}_3\text{O}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2$
cluster using Platinum electrode.

Figure 40. Cyclic Voltammogram of $\text{Mo}_2\text{WO}_2(\text{OAc})_6(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2$
cluster using Platinum electrode.
The spectra clearly show that the same trinuclear species i.e. \( W_3O_2(O_2CCH_3)_6(H_2O)_3^{2+} \) are present in MeOH and EMIBF\(_4\) solution and that the trinuclear structure of the clusters did not change by dissolving \( W_3O_2(O_2CCH_3)_6(H_2O)_3(CF_3SO_3)_2 \) in ionic liquid. A cyclic voltammogram of \( W_3O_2(O_2CCH_3)_6(H_2O)_3(CF_3SO_3)_2 \) is shown in Figure 39. The voltammogram is very similar to the voltammogram of \( Mo_2WO_2(OAc)_6(H_2O)_3(CF_3SO_3)_2 \) obtained in ionic liquid. On the initial negative sweep it displays two small reduction peaks. At ~1.8 V cathodic current increases and upon reversal of the potential a large reoxidation wave at \( I_{pa} = -0.2 \) V is obtained. This voltammogram is very similar to the one obtained for \( Mo_2WO_2(OAc)_6(H_2O)_3(CF_3SO_3)_2 \) cluster indicating that the deposition of Tungsten metal has occurred. Cyclic voltammograms of \( W_3O_2(O_2CCH_3)_6(H_2O)_3(CF_3SO_3)_2 \) and \( Mo_2WO_2(OAc)_6(H_2O)_3(CF_3SO_3)_2 \) are shown in Figures 39 and 40.
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