Ni complexes. While the M–Se distances and internal Se–M–Se angles vary considerably within the series M = Pt, Ni, and Mo, the other angles within the five-membered metal–ligand chelate ring show relatively minor variations. The insensitivity of the ligand geometry to the size and/or coordination number of the central metal ion is highlighted by considering the nonbonding intramolecular Se···Se contacts. While the interligand Se···Se distances vary from 3.356 (3) to 3.121 (5) Å, the corresponding intraligand Se···Se distances, which reflect the chelate bite of the ligands, fall within the more limited range of 3.345 (3)–3.256 (6) Å. Thus, the tds ligands appear to adjust to different bonding situations by altering the M–Se distances while maintaining a relatively constant bite; the preferred ligand geometry apparently is determined by the importance of π-bonding in the highly delocalized electronic structures of these complexes.

Acknowledgment. We thank Dr. M. J. Natan for assistance with the electrochemical measurements. This work was supported by the Solid State Chemistry Program of the National Science Foundation (Grant DMR 85-19233 to B.M.H.); it benefited from the Northwestern University Materials Research Center under the NSF-MRL program (Grant DMR 85-20280). We further acknowledge Johnson Matthey Inc. for the loan of platinum salts.

Registry No. I (E = Se), 17744-01-3; $[(C_4H_9)_4N][Ni(tds)_2]$, 110304-00-2; $[(C_4H_9)_4N]_2[Ni(tds)_2]$, 113352-30-0; $[Ni(tds)_2]$, 28951-67-9; $[Cu(tds)_2]^-$, 47421-83-0; $[Cu(tds)_2]^{2-}$, 47451-04-7; $[Cu(tds)_2]$, 113378-58-8; $[(C_9H_5)_4P][Cu(tds)_2]$, 113352-38-8; $[Pt(tds)_2]^-$, 102764-51-2; $[Pt(tds)_2]^{2-}$, 113352-31-1; $[Pt(tds)_2]$, 113378-33-9; $[(C_6H_5)_4P][Pt(tds)_2]$, 113352-36-6; $[(C_6H_5)_4P]_2[Pt(tds)_2]$, 113352-37-7; $[(C_4H_9)_4N][Au(tds)_2]$, 113352-33-3; $[Au(tds)_2]^{2-}$, 113352-34-4; $[Au(tds)_2]$, 113352-35-5; $(Ph_3P)_2NiCO_2$, 13007-90-4; $(Ph_3P)_2PtCl_2$, 10199-34-5; $(Ph_3P)CuI$, 47107-74-4; $(Ph_3P)AlCl$, 14243-64-2.

Supplementary Material Available: Listings of all distances and angles, hydrogen atom parameters, and temperature factors (4 pages); a listing of calculated and observed structure factors (33 pages). Ordering information is given on any current masthead page.

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Electrochemistry of Molybdenum Chloride Dimers in a Basic Ambient-Temperature Molten Salt

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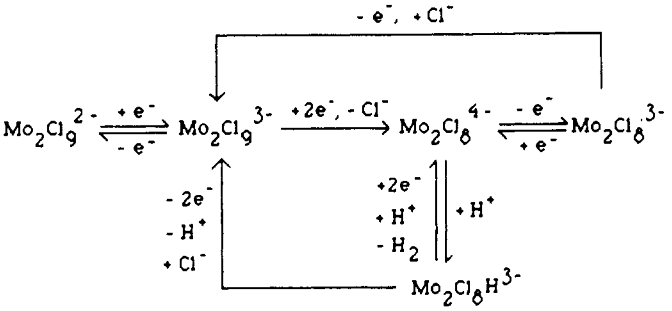
The molybdenum(III) dimers $Mo_2Cl_9^{3-}$ and $Mo_2Cl_8H^{3-}$ and the molybdenum(II) dimer $Mo_2Cl_8^{4-}$ have been studied in the basic ambient-temperature molten salt $AlCl_3$–1-methyl-3-ethylimidazolium chloride (ImCl) by employing electrochemistry and visible spectroscopy. Both Mo(III) dimers are reduced to the Mo(II) dimer at approximately the same potential in a single, irreversible, two-electron step. The quadruply bonded dimer, $Mo_2Cl_8^{4-}$, undergoes a quasi-reversible, one-electron oxidation to $Mo_2Cl_8^{3-}$ and is further oxidized to $Mo_2Cl_9^{3-}$ in an irreversible, one-electron step at a more anodic potential. The hydride dimer $Mo_2Cl_8H^{3-}$ undergoes an irreversible, two-electron oxidation that produces $Mo_2Cl_9^{3-}$ and a proton. The electrochemical and chemical interconversions of the dimers are summarized as follows:



Introduction

Mixtures of $AlCl_3$ and 1-methyl-3-ethylimidazolium chloride (ImCl) form molten salts that remain liquid at ambient temperatures over a wide range of compositions.[1] Compositions with $AlCl_3$:ImCl molar ratios <1.0 are termed basic since chloride ion, a weak Lewis acid, is in excess, and the dominant anion species are chloride and tetrachloroaluminate, $AlCl_4^-$. Compositions with $AlCl_3$:ImCl molar ratios >1.0 are termed acidic, since excess $AlCl_3$ results in the formation of the strong Lewis acid $Al_2Cl_7^-$, and the dominant anion species are $Al_2Cl_7^-$ and $AlCl_4^-$. The wide electrochemical windows available in these molten salts make them attractive solvents for electrochemical examination of both inorganic and organic species.[1] In the basic melt, the anodic limit is determined by chloride oxidation, and the cathodic limit is set by reduction of the imidazolium cation. In the acidic melt, the anodic limit is determined by the oxidation of the $AlCl_4^-$ anion, and the cathodic limit is set by reduction of the $Al_2Cl_7^-$ anion to Al metal.[1]

In group VIa, both molybdenum and tungsten chloride complexes have been studies in the basic 0.8:1.0 $AlCl_3$:ImCl melt. Hexachloromolybdate monomers were found to exhibit a quasi-reversible Mo(III)/Mo(IV) redox couple.[2] In the case of tungsten, both the hexachlorotungstate monomers and the nonachloroditungstate(III) dimer, $W_2Cl_9^{3-}$, have been studied.[3] The hexachlorotungstate monomeric species exhibited two quasi-reversible redox couples, a W(III)/W(IV) couple and a W(IV)/W(V) couple. The electrochemistry of the tungsten dimer was more complex and involved dissociation into monomeric species.[3]

To extend the electrochemical studies of the group VIa metals, we undertook a study of the molybdenum dimer species $Mo_2Cl_9^{3-}$, $Mo_2Cl_8H^{3-}$, and $Mo_2Cl_8^{4-}$ in the basic melt. In the first two

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dimers, the molybdenums are in the +3 oxidation state, and the geometry of both dimers is that of a face-sharing bioctahedron. In $Mo_2Cl_9^{3-}$, three chloride ligands form the bridge between metal centers, and the Mo–Mo separation varies from 2.52 Å for the K^+ salt to 2.78 Å for the Me_4N^+ salt.[4,5] This variation in the Mo–Mo distance for different $Mo_2Cl_9^{3-}$ salts is due to crystal-packing effects.[4] In $Mo_2Cl_8H^{3-}$, the bridge between metal centers consists of two chloride ligands and one hydride ligand, and the Mo–Mo separation is 2.38 Å.[5,6] The $Mo_2Cl_8^{4-}$ dimer is of course the well-known Mo(II)–Mo(II) dimer in which no bridging ligands are present; instead, the metal centers are joined through a short Mo–Mo quadruple bond of length 2.14 Å.[5,7]

Experimental Section

ImCl was synthesized as previously described.[8] Melts were prepared by gradual addition of small quantities of sublimed $AlCl_3$ (Fluka) to ImCl with stirring until the desired mole ratio was obtained.

All experiments were performed under a purified He atmosphere in a Vacuum Atmospheres drybox with an HE 493 Dri Train.

An IBM electrochemical cell was used. The glassy carbon (GC) working electrode (area 0.071 cm^2) consisted of a 3-mm-diameter GC rod sealed in a glass tube. The Pt working electrode (area 0.020 cm^2), purchased from Bioanalytical Systems, consisted of a 1.6-mm-diameter Pt disk sealed in Kel-F. Reticulated vitreous carbon (RVC) was obtained from Normar Industries, Anaheim, CA. The reference and counter electrodes consisted of Al wire immersed in acidic 1.5:1.0 $AlCl_3$:ImCl melts contained in separate fritted tubes isolated from the analyte solution.

Cyclic voltammetric experiments were performed by using a system consisting of an EG&G PARC Model 173 potentiostat/galvanostat with a 175 universal programmer and a Houston Instruments Model 200 X-Y recorder. Pulse voltammetric experiments were performed with a computer-controlled system similar to that described elsewhere.[9]

The molybdenum dimers used in this study were prepared from MoO_3 by the procedures described by Bino and Gibson.[10] Mo(VI) was reduced electrolytically in aqueous HCl (12 M) to produce $MoCl_6^{3-}$, which was then condensed to $Mo_2Cl_9^{3-}$ by evaporating the solvent almost to dryness with a rotoevaporator. The $Mo_2Cl_9^{3-}$ salt was isolated at this point by addition of $(n\text{-Bu})_4NCl$ to the concentrated solution. The Mo(II) dimers were synthesized as described by Bino and Gibson[10] by using Zn(Hg) to reduce the $Mo_2Cl_9^{3-}$ dimer. A small modification to the literature preparation was made. Instead of the $Mo_2Cl_9^{3-}$ solution being passed through a Jones reductor, the Zn(Hg) granules were added to the solution, which was then agitated by rotating on the rotoevaporator. After the Mo dimer had been completely reduced, ca. 10 min, the solution was filtered to remove the Zn(Hg) granules, and the filtrate was treated as in the literature preparation to give the desired Mo(II) dimer.[10]

Visible absorption spectra were obtained by using a Tracor Northern 6500 spectrophotometer equipped with a photodiode array detector. All spectra were obtained with the use of a 1 mm path length cell.

Experiments were performed at ambient temperature, ca. 22 °C.

Results and Discussion

Cyclic voltammetry and normal-pulse voltammetry were performed by using the GC electrode unless stated otherwise. This was done because protonic impurities in the basic melt are reduced to H_2 with an $E_{1/2}$ value of −0.42 V at a Pt electrode,[11] thus obscuring a portion of the electrochemical window and possibly interfering with the electrochemistry of the dimer being studied. At a GC electrode no electrochemistry for protons is seen.[11] Protonic impurities are difficult to avoid since they can be introduced into the melt from a number of sources including trace amounts of water present in the hygroscopic ImCl salt, hydrolysis products of the $AlCl_3$ formed during its workup and storage, and protonic impurities present in the $(Bu_4N)_3Mo_2Cl_9$ salt.[12]

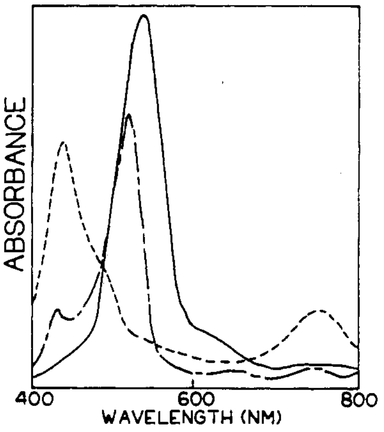

Figure 1. Visible absorption spectra for Mo dimers in basic 0.8:1.0 $AlCl_3$:ImCl melt: (-—-) $Mo_2Cl_9^{3-}$; (—) $Mo_2Cl_8^{4-}$; (---) $Mo_2Cl_8H^{3-}$. Spectra are normalized in concentration.

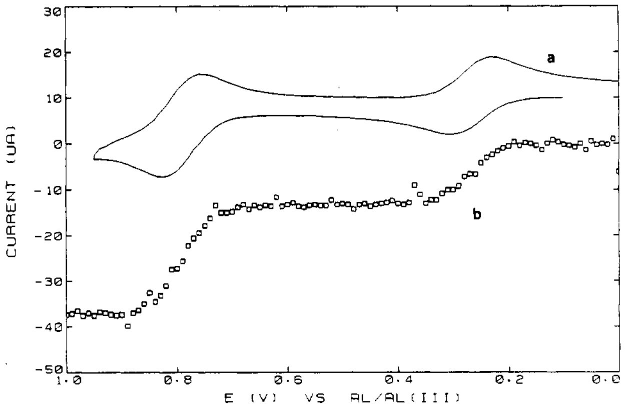

Figure 2. Oxidation of 8.5 mM $Mo_2Cl_9^{3-}$ (5 mM $MoCl_6^{3-}$ impurity) in basic 0.8:1.0 $AlCl_3$:ImCl melt on GC: (a) cyclic voltammogram, v = 50 mV/s; (b) normal-pulse voltammogram, t_p = 250 ms.

Table I. Visible Absorption Data for Molybdenum Chloride Dimers

solute	solvent	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	ref
$Mo_2Cl_9^{3-}$	0.8:1.0 melt[a]	435 (160), 527 (560), 655 (10), 758 (20)	this work
$Mo_2Cl_9^{3-}$	CH_2Cl_2	429 (573), 528 (638), 649 (33), 741 (25), 758 (23)	13
$Mo_2Cl_8^{4-}$	0.8:1.0 melt[a]	534 (740)	this work
$Mo_2Cl_8^{4-}$	6 M HCl	518 (340)	21
$Mo_2Cl_8H^{3-}$	0.8:1.0 melt	454 (460), 517 (sh),[b] 748 (180)	this work
$Mo_2Cl_8H^{3-}$	8 M HCl	424 (1900), 515 (135), 758 (110)	25
$MoCl_6^{3-}$	0.8:1.0 melt	439 (36), 544 (30)	2

[a] Treated to condense the monomer impurities to the dimer. [b] Shoulder is probably due to the presence of a small quantity of $Mo_2Cl_8^{4-}$.

A. $Mo_2Cl_9^{3-}$ Electrochemistry. A solution of $Mo_2Cl_9^{3-}$ in a basic 0.8:1.0 $AlCl_3$:ImCl melt was prepared by dissolving the Mo(III) salt $(Bu_4N)_3Mo_2Cl_9$ in the melt at ambient temperature. A pink solution resulted with a visible spectrum characteristic of the dimer species as seen in Figure 1 and Table I.[13] A cyclic voltammogram

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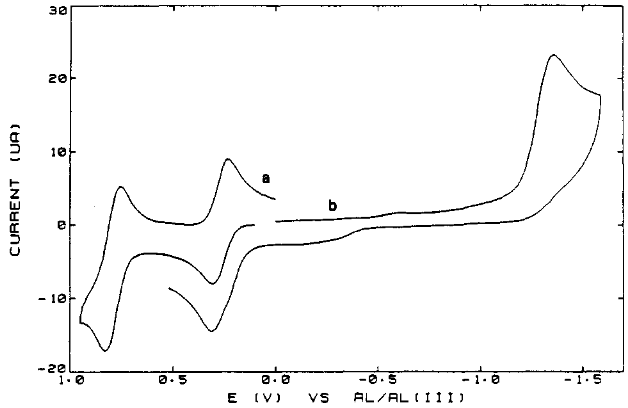

Figure 3. Cyclic voltammogram of 8.5 mM $Mo_2Cl_9^{3-}$ (5 mM $MoCl_6^{3-}$ impurity) in basic 0.8:1.0 $AlCl_3$:ImCl melt on GC (v = 50 mV/s). Initial scan direction: (a) anodic; (b) cathodic.

Table II. Cyclic Voltammetric Parameters for Oxidation of 12 mM $Mo_2Cl_9^{3-}$ in Slightly Basic $AlCl_3$–ImCl on Glassy Carbon

scan rate (v), mV/s	E_p^a, V	ΔE_p, mV	i_p^a/i_p^c[a]	$i_p^a/v^{1/2}$, mA cm^{-2} V$^{-1/2}$ s$^{1/2}$
10	0.843	60	1.06	0.824
20	0.847	64	1.13	0.810
50	0.849	63	1.12	0.806
100	0.847	64	1.05	0.886
200	0.852	72	1.33[b]	0.727

[a] $i_p^a/i_p^c = 1/[(i_p^c)_0/i_p^a + 0.485(i_{sp})_0/i_p^a + 0.086]$.[15] [b] This large i_p^a/i_p^c value is due to difficulties in background subtraction at potentials near the melt anodic limit.

and a normal-pulse voltammogram at the GC electrode showing the oxidation waves for a solution of $Mo_2Cl_9^{3-}$ in the basic 0.8:1.0 $AlCl_3$:ImCl melt are presented in Figure 2. The oxidation wave at 0.32 V corresponds to the one-electron oxidation of the Mo(III) monomer $MoCl_6^{3-}$ to the Mo(IV) monomer $MoCl_6^{2-}$.[2] The literature E_p^a value for this monomer oxidation is ca. 0.35 V.[2,14] The presence of the monomer apparently results from incomplete condensation during the aqueous synthesis of $Mo_2Cl_9^{3-}$. For $Mo_2Cl_9^{3-}$, therefore, only one oxidation wave at 0.85 V is observed. As shown in Table I, the visible spectra of the monomer and the dimer are similar, and the extinction coefficients for the monomer are small. Therefore, the visible spectrum of the melt did not indicate the presence of the monomer.

A cyclic voltammogram showing all the redox waves for the $Mo_2Cl_9^{3-}$ solution is shown in Figure 3. In addition to the oxidation waves discussed above, one reduction wave at ca. −1.4 V is seen. After scanning cathodically into the reduction wave and then reversing the scan anodically, we observed a new oxidation wave near −0.3 V.

The $MoCl_6^{3-}$ impurity could be condensed to $Mo_2Cl_9^{3-}$ by adding enough $AlCl_3$ to produce an acidic melt. The desired basic melt was then obtained by adding the appropriate quantity of ImCl. This condensation is very similar to that used above for the synthesis of $Mo_2Cl_9^{3-}$ from aqueous solution. The dimer thus formed showed no evidence of dissociation in the basic melt at room temperature over several days.

(1) Oxidation of $Mo_2Cl_9^{3-}$. A solution of $Mo_2Cl_9^{3-}$ was prepared by first dissolving $(Bu_4N)_3Mo_2Cl_9$ in a slightly basic melt; $AlCl_3$ was added to produce a slightly acidic melt; finally, enough ImCl was added to again produce a slightly basic melt. A cyclic voltammogram of the resulting 12 mM $Mo_2Cl_9^{3-}$ solution showed nearly complete conversion of the monomer to the dimer; i.e., the monomer oxidation wave at 0.32 V was essentially eliminated. Cyclic voltammetric parameters, scan rates (v), anodic peak potentials (E_p^a), anodic and cathodic peak potential separations ($\Delta E = E_p^a - E_p^c$), anodic to cathodic peak current ratios (i_p^a/i_p^c), and the ratio $i_p^a/v^{1/2}$, for the oxidation of $Mo_2Cl_9^{3-}$ in this slightly basic melt, are summarized in Table II. For scan rates from 10 to 100 mV/s, the peak separations are near the theoretical value for a reversible one-electron process, 56 mV, and E_p^a does not shift. The oxidation process, therefore, is reversible over these scan rates and is a one-electron process.[15] The peak current i_p for a reversible process is given by

$$i_p = (2.68 \times 10^5)n^{3/2}AD^{1/2}v^{1/2}C \qquad (1)$$

where v is the scan rate and the other terms are the same as defined above.[15] A plot of i_p vs $v^{1/2}$ yields a straight line; from the slope of this line, a diffusion coefficient of 8.0 × 10^{-8} cm^2/s is calculated for $Mo_2Cl_9^{3-}$ in the slightly basic melt at 22 °C.

Table III. Normal-Pulse Voltammetric Parameters for Oxidation of 12 mM $Mo_2Cl_9^{3-}$ in Slightly Basic $AlCl_3$–ImCl Melt in Glassy Carbon

t_p, ms	$E_{1/2}$, V	$i_l t_p^{1/2}$, mA cm^{-2} s$^{1/2}$	E vs. log $[(i_l - i)/i]$ slope, mV
250	0.828	0.172	59
500	0.823	0.163	58
1000	0.824	0.163	60
2000	0.816	0.146	66

The oxidation of $Mo_2Cl_9^{3-}$ was also analyzed by using normal-pulse voltammetry. Potential steps of 10 mV were used in these oxidation studies. Between each pulse, the surface concentration of the Mo(III) dimer was returned to its original concentration by holding the potential at −0.15 V for 2 s while the melt was stirred. The solution was then permitted to stand without stirring for 5 s. Normal-pulse voltammetric parameters, pulse widths (t_p), $E_{1/2}$ values, the products $i_l t_p^{1/2}$ (i_l = limiting current), and the slopes of the E vs log $[(i_l - i)/i]$ plots for the oxidation of $Mo_2Cl_9^{3-}$ in the slightly basic melt are given in Table III. Relatively long pulse widths were used since at shorter pulse widths the oxidation wave begins to show quasi-reversible behavior. The plot of i_l vs $t_p^{-1/2}$ is linear and intercepts the origin, indicating the limiting currents are diffusion controlled.[16] For a reversible process, the slope of an E vs log $[(i_l - i)/i]$ plot should have the value $58/n$ mV, where n is the number of electrons involved in the process.[16] For the pulse widths in Table III, the slope values are approximately 58 mV, confirming the oxidation to be a one-electron process.

The diffusion coefficient, D, for $Mo_2Cl_9^{3-}$ can be calculated from the diffusion-controlled-limiting-current equation for a normal pulse experiment

$$i_l = nFAC(D/\pi t_p)^{1/2} \qquad (2)$$

where n is the number of electrons involved in the process, F is the Faraday constant, A is the area of the working electrode, C is the concentration of the electroactive species, and t_p is the pulse width.[16] By the application of eq 2, a plot of i_l vs. $t_p^{-1/2}$ yields a D value of 7.9 × 10^{-8} cm^2/s, in agreement with that determined from the cyclic voltammetric data.

The dimer diffusion coefficient is related to the melt viscosity by the Stokes–Einstein relation

$$D = kT/6\pi\eta r \qquad (3)$$

where k is the Boltzmann constant, r is the radius of the diffusing species, and η is the absolute viscosity of the melt. The viscosity of a slightly basic melt at 22 °C is approximately the same as a basic 0.8:1.0 $AlCl_3$:ImCl melt at 40 °C.[17] Therefore, the literature D value of 1.5 × 10^{-7} cm^2/s determined for $W_2Cl_9^{3-}$ in an 0.8:1.0 $AlCl_3$:ImCl melt at 40 °C should be comparable to the D value for $Mo_2Cl_9^{3-}$ determined here.[3] It appears the D value

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(14) All potentials in ref 2 and 3 are referenced to an Al wire in a 2:1 melt; therefore, 150 mV was added to the potential data in ref 2 and 3 to reference the values to an Al wire in a 1.5:1.0 melt used as a reference electrode in this work.

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of 8×10^{-8} cm^2/s for $Mo_2Cl_9^{3-}$ determined here is a little low compared to the value for $W_2Cl_9^{3-}$ at 40 °C in a basic 0.8:1.0 melt. It should be noted that the D values determined in this study may not be as accurate as those found in the literature for $W_2Cl_9^{3-}$ because of the need to manipulate the melt to remove the monomer impurity. This procedure increases the error in the value of the $Mo_2Cl_9^{3-}$ concentration used to calculate the D value.

Since $E_{1/2}$ values can be related to the energies of the HOMOs when complexes of similar configuration are considered, the oxidation potentials for the related Mo and W dimers and monomers can be compared.[18,19] Direct comparison of the oxidation potentials for Mo and W monomers or dimers is not very informative since third-row transition elements are more stable in higher oxidation states than are second-row transition metals. Therefore, $MoCl_6^{3-}$ with an $E_{1/2}$ value of 0.27 V (value from this work) is oxidized at a more anodic potential than is WCl_6^{3-} with an $E_{1/2}$ value of −0.65 V.[3,14] The values that are worthy of comparison are the potential shifts in the oxidation potentials caused by condensation of the monomers to their respective dimers. Since the electron removed in the dimer oxidation is situated in a molecular orbital participating in the metal–metal bonding, this anodic shift should provide information regarding the orbital energy changes that occur upon condensation of the monomers.

The bonding in these dimers has been described by Hoffmann and Summerville, using extended Hückel calculations.[20] The metal–metal bonding orbitals are formed from the interaction of t_{2g} orbitals originally present as nonbonding orbitals on the octahedrally coordinated monomers. The metal–metal bonds formed upon condensation consist of one σ bond and two π bonds. The π bonds are degenerate and are higher in energy than the σ bond. The one electron removed upon oxidation of a dimer is taken from one of these π-bonding orbitals. Additionally, the electron removed upon oxidation of the monomer comes from the nonbonding t_{2g} orbitals, which are used to form the metal–metal bonding orbitals. Therefore, the anodic shift of the oxidation potential resulting from monomer condensation can be taken as an indication of the stabilization afforded by formation of the dimer. The initial one-electron oxidation of the W(III) dimer occurs at an $E_{1/2}$ value of +0.07 V.[3,14] The shift in the oxidation potential upon condensation is 0.53 V for Mo(III) and 0.72 V for W(III); thus, the metal–metal π bonding stabilizes the W(III) dimer more than it does the Mo(III) dimer.

This greater metal–metal bonding stabilization in the W(III) dimer is evidenced structurally in the shorter metal–metal distance in the W(III) dimer: 2.50 Å in $Cs_3W_2Cl_9$ versus 2.65 Å in $Cs_3Mo_2Cl_9$.[4] The Cs^+ salts are compared so that crystal-packing effects are the same for each anion structure; therefore, the changes in the M–M distances are due to M–M bonding interactions alone. Additionally, for the idealized face-shared bioctahedral structure of these dimers, the M–Cl(bridge)–M angle is expected to be 70.5°. In $Cs_3W_2Cl_9$, this angle is compressed to 61° by the W–W bonding while it is compressed only to 65° in $Cs_3Mo_2Cl_9$. It is interesting to note that for the Cr(III) dimer, $Cs_3Cr_2Cl_9$, where no metal–metal interaction is seen, the Cr–Cr separation is 3.12 Å and the Cr–Cl_b–Cr angle is expanded to 76.5°, indicating a repulsion of the metal centers.[5,20] In the melts, the M–M distances are not known; however, it is reasonable to assume the same trends in M–M bonding occur in the melts as in the solid state.

Efforts to produce quantitatively the one-electron-oxidized species $Mo_2Cl_9^{2-}$ by electrolyzing $Mo_2Cl_9^{3-}$ in basic 0.8:1.0 melt at a potential of 0.95 V were unsuccessful. The visible spectrum of the solution after partial electrolysis did not resemble that of $Mo_2Cl_9^{2-}$, which has been prepared by a condensation reaction employing $MoCl_6^-$ and $Mo(CO)_4Cl_3^-$.[13] Cyclic voltammetry on the electrolyzed solution showed only monomeric Mo species to be present. This production of monomeric species was also seen for the attempted one-electron electrolysis of $W_2Cl_9^{3-}$.[3] Although $Mo_2Cl_9^{2-}$ can be prepared chemically,[13] it does not appear to be stable in the melt on the time scale needed to carry out a bulk electrolysis.

Table IV. Cyclic Voltammetric Parameters for Reduction of 12 mM $Mo_2Cl_9^{3-}$ in Slightly Basic $AlCl_3$–ImCl on Glassy Carbon

scan rate (v), mV/s	E_p^c, V	$E_p - E_{p/2}$, mV	$i_p^c/v^{1/2}$ mA cm^{-2} V$^{-1/2}$ s$^{1/2}$
10	−1.276	85	1.61
20	−1.285	83	1.54
50	−1.312	78	1.31
100	−1.349	94	1.27
200	−1.379	101	1.06

Table V. Normal-Pulse Voltammetric Parameters for Reduction of 12 mM $Mo_2Cl_9^{3-}$ in Slightly Basic $AlCl_3$–ImCl Melt on Glassy Carbon

t_p, ms	$E_{1/2}$, V	$i_l t_p^{1/2}$, mA cm^{-2} s$^{1/2}$	t_p, ms	$E_{1/2}$, V	$i_l t_p^{1/2}$, mA cm^{-2} s$^{1/2}$
250	−1.261	0.394	1000	−1.308	0.338
500	−1.302	0.349	2000	−1.323	0.337

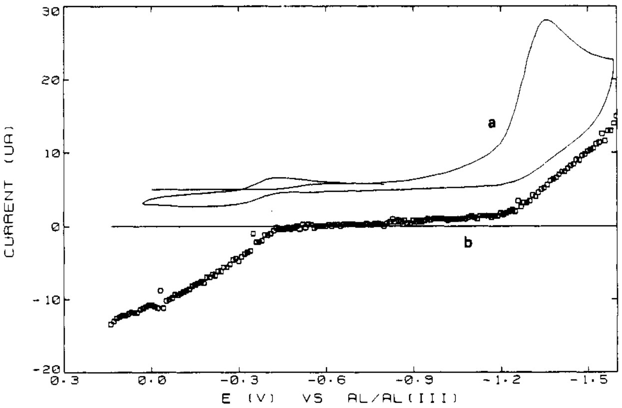

Figure 4. Two-electron reduction of 8.5 mM $Mo_2Cl_9^{3-}$ and initial one-electron oxidation of the reduction product $Mo_2Cl_8^{4-}$ in basic 0.8:1.0 $AlCl_3$:ImCl melt on GC: (a) cyclic voltammogram, v = 50 mV/s; (b) reverse-normal-pulse voltammogram, τ = 2 s at −1.6 V and t_p = 250 ms.

(2) Reduction of $Mo_2Cl_9^{3-}$. The single reduction wave seen in Figure 3 was analyzed for the 12 mM solution of $Mo_2Cl_9^{3-}$ in the slightly basic melt, which had been treated as described above to condense monomer to dimer. The relevant parameters are summarized in Tables IV and V. For the normal-pulse experiments, pulses shorter than 100 ms give ill-defined waves for which the current continually increases without achieving a limiting plateau. The peak potential for the cyclic voltammetry undergoes a large cathodic shift, and $i_p^a/v^{1/2}$ values decrease as the scan the rate is increased. With increasing scan rate, the peak in the cyclic voltammogram becomes broadened. These results, particularly the cyclic voltammetric results, imply that at a GC electrode the reduction of the dimer is a multistep process that may involve more than one electron-transfer step and/or chemical rearrangement.[15] The quality of the data is insufficient to postulate a detailed mechanism.

Despite the apparent complex nature of the reduction process, the diffusion-controlled limiting currents obtained in the normal-pulse experiments can be used to determine the number of electrons involved in the reduction process. For $Mo_2Cl_9^{3-}$ in the slightly basic melt, the average ratio of the $i_l t^{1/2}$ values for the reduction to those for the oxidation is close to 2 (Tables III and V). Referring to eq 2, one sees that all the terms, except n, are the same for both the reduction process and the oxidation process. Therefore, the n value for the reduction process must be 2. Addition of ImCl to the slightly basic melt, converting it to a basic 0.8:1.0 melt, caused the limiting plateaus for the reduction waves to become poorly defined. Apparently a large excess of chloride either complicates or inhibits the reduction process. This accounts for the apparent n value of less than 2 observed in basic 0.8:1.0 melt.

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Table VI. Reverse-Normal-Pulse Parameters for Reduction of 8.5 mM $Mo_2Cl_9^{3-}$ in Basic 0.8:1.0 $AlCl_3$:ImCl Melt in Glassy Carbon

τ, s	t_p, ms	i_{DC}, mA cm^{-2}	i_{RP}, mA cm^{-2}	n_{DC}/n_{RP}^{a}
2.05	50	0.10	−0.215	2.5
2.10	100	0.13	−0.156	2.9
2.25	250	0.10	−0.113	1.8
2.50	500	0.10	−0.061	2.1
10.05	50	0.062	−0.298	2.7
10.10	100	0.056	−0.203	2.5
10.50	500	0.066	−0.130	1.8

^{a}Average value of 2.3 with standard deviation of 0.4.

As shown in Figure 4a, reversing the scan direction of the cyclic voltammogram following the two-electron reduction revealed a new quasi-reversible oxidation wave at −0.3 V for the product of the reduction. A second irreversible oxidation wave for the reduction product was seen at ca. 0.3 V in the slightly basic melt. In melts containing Mo(III) monomer impurities, this second oxidation appeared only as a shoulder on the monomer oxidation wave.

To identify the reduction product, electrolysis of 8.5 mM $Mo_2Cl_9^{3-}$ in a basic 0.8:1.0 melt at −1.6 V was performed by employing a Pt-flag electrode. The solution was not, however, treated to remove the Mo(III) monomer; therefore, the solution contained 5 mM $MoCl_6^{3-}$. Before reduction of the dimer, the potential was held at −1.25 V to remove protonic impurities, which are reduced to H_2 on Pt at an $E_{1/2}$ of −0.45 V.[11] During reduction of the dimer at −1.6 V, the melt changed from pink to dark red. The visible spectrum of the reduction product showed an absorption maximum at 534 nm (Figure 1 and Table I) characteristic of the quadruply bonded Mo(II) dimer, $Mo_2Cl_8^{4-}$.[21] The absorption corresponds to the well-known $\delta \rightarrow \delta^*$ transition.[22] Because remaining protonic impurities were also electrolyzed at the Pt-flag electrode, it was not possible to quantitate the electrolysis to confirm the n value of 2 for the reduction process.

Prior to electrolysis of the 8.5 mM $Mo_2Cl_9^{3-}$ solution in the 0.8:1.0 melt at −1.6 V, reverse-normal-pulse experiments were performed on the Mo(III) dimer.[23] Generation pulse widths (τ) of 2 and 10 s at a potential of −1.6 V were used to produce $Mo_2Cl_8^{4-}$ during the generation pulse. The analysis pulse was shifted anodically in 25-mV steps. Between each pair of generation and analysis pulses, the GC electrode was returned to its original conditions by holding its potential at −0.15 V while the melt was stirred for 2 s and was then held unstirred for 5 s, allowing the convection currents to dissipate. A reverse-normal-pulse voltammogram showing the reduction of $Mo_2Cl_9^{3-}$ and the first oxidation of $Mo_2Cl_8^{4-}$ is seen in Figure 4b. The parameters for the reverse-normal-pulse experiments, time used for initial reduction (τ), analysis pulse width (t_p), diffusion-limited current for the reduction process (i_{DC}), diffusion-limited current for the oxidation process (i_{RP}), and the ratio of the number of electrons in each process (n_{DC}/n_{RP}), are summarized in Table VI. The ratio of the number of electrons for the reduction (n_{DC}) to the number of electrons for the oxidation of the reduction product (n_{RP}) is given by eq 4.[23] From normal-pulse voltammetric results for the

$$i_{DC}/i_{RP} = n_{DC}/n_{RP}[((\tau + t_p)/t_p)^{1/2} - 1] \qquad (4)$$

reduction process, it has been shown that $n_{DC} = 2$; thus, n_{RP} for the first $Mo_2Cl_8^{4-}$ oxidation wave in Figure 4b is 1. The variability in the n_{DC}/n_{RP} values is due to difficulties in determining the limiting currents.

The potential for the dimer reduction in the molten salt is quite cathodic, ca. 1 V, of the reduction potential for protons.[11] This is interesting because, in the chemical reduction of $Mo_2Cl_9^{3-}$ to the quadruply bonded dimer in aqueous solution,[10] the Zn(Hg) used in the reduction generates a considerable amount of hydrogen while it also reduces the Mo(III) dimer. It was observed in the aqueous preparation that if the Mo(II) dimer being produced was allowed to remain in solution long enough for the hydrogen generation to diminish, then the Mo(II) dimer was oxidized to the Mo(III) dimer $Mo_2Cl_8H^{3-}$. This is not unexpected since the usual preparation of $Mo_2Cl_8H^{3-}$ involves warming $Mo_2Cl_8^{4-}$ in aqueous HCl.[6] Apparently, in this chemical preparation in aqueous solution there is a fine balance preventing reoxidation of the Mo(II) dimer. Consistent with this view, the first oxidation wave for $Mo_2Cl_8^{4-}$ in the molten salt is found at ca. −0.3 V, very near the redox couple for H^+/H_2.[11]

Table VII. Cyclic Voltammetric Parameters for First Oxidation of 8.5 mM $Mo_2Cl_8^{4-}$ in Basic 0.8:1.0 $AlCl_3$:ImCl Melt on Glassy Carbon

scan rate (v), mV/s	E_p^a, V	E_p^c, V	ΔE_p, mV^a	i_p^a/i_p^c	$i_p^a/v^{1/2}$, mA cm^{-2} V$^{-1/2}$ s$^{1/2}$
10	−0.242	−0.405	163	2.1	0.352
20	−0.229	−0.380	161	1.8	0.329
50	−0.220	−0.410	190	1.6	0.286
100	−0.212	−0.412	202	1.7	0.263
200	−0.190	−0.422	232	1.6	0.204

^{a}E_0(av) is −0.313 (±0.007) calculated as $E_p - \Delta E_p/2$.

B. Electrochemistry of $Mo_2Cl_8^{4-}$. To study the electrochemistry of $Mo_2Cl_8^{4-}$ in the basic 0.8:1.0 $AlCl_3$:ImCl melt, both $Mo_2(OAc)_4$ (OAc = acetate) and $K_4Mo_2Cl_8$ were prepared.[10] Introduction of $Mo_2(OAc)_4$ into the melt resulted in the formation of a dark red solution as the acetate dissolved. The visible spectrum of the newly prepared solution confirmed it to be the anion $Mo_2Cl_8^{4-}$.[21] The reaction

$$Mo_2(OAc)_4 + 4AlCl_4^- + 4Cl^- \rightarrow Mo_2Cl_8^{4-} + 4AlCl_3(OAc)^- \qquad (5)$$

has been used previously to prepare other Mo halide species.[24] The visible spectrum of the newly prepared solution confirmed it to be the anion $Mo_2Cl_8^{4-}$.[21] Cyclic voltammetry on this solution, however, proved to be confusing and variable. The solution was observed to gradually take on a yellow-green color. The visible spectrum of the melt solution after several hours showed that the $Mo_2Cl_8^{4-}$ anion was being oxidized to the hydride species $Mo_2Cl_8H^{3-}$ by the protonic impurities in the melt.[25]

Efforts to introduce $K_4Mo_2Cl_8$ into the basic melt were thwarted by the apparent insolubility of this species in the melt. In an acidic melt, the $K_4Mo_2Cl_8$ was observed to react, producing a brown solid. Upon conversion of the acid melt back to a basic melt by addition of ImCl, the solid dissolved; however, the $Mo_2Cl_8^{4-}$ anion had been nearly quantitatively converted to $Mo_2Cl_8H^{3-}$. The proton impurities apparently rapidly oxidized the Mo(II) dimer in an acidic melt, whereas this oxidatioin is slow in a basic melt.

Due to the difficulties resulting from the presence of protonic impurities in the melt, it was necessary to study the $Mo_2Cl_8^{4-}$ produced by the complete electrolytic reduction of $Mo_2Cl_9^{3-}$, described above, in which the Mo(III) dimer was reduced at a potential of −1.6 V by using a Pt-flag electrode. Since this reduction was carried out at a Pt-flag electrode, nearly all protons were also removed from the solution. Thus produced, the $Mo_2Cl_8^{4-}$ dimer was stable for several days in the basic melt.

The cyclic voltammetric results for the first $Mo_2Cl_8^{4-}$ oxidation wave in the 0.8:1.0 melt are summarized in Table VII. The ΔE_p values are quite large, and the anodic wave at ca. −0.22 V is broad with a peak potential (E_p^a) that shifts anodically with increasing scan rate. The corresponding reduction wave is much better defined and does not shift as much as does the anodic wave with increasing scan rate. Also, the ratio of the current of the anodic peak to that of the cathodic peak is considerably greater than 1, indicating a subsequent reaction of the one-electron-oxidized product or the presence of another oxidation process occurring concurrently with the first oxidation of $Mo_2Cl_8^{4-}$.

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Table VIII. Summary of Pulse Parameters for Redox of 8.5 mM $Mo_2Cl_8^{4-}$: Normal Pulse and Reverse Normal Pulse (τ = 5 s) on Glassy Carbon[a]

	normal pulse		reverse normal pulse	
t_p, ms	$E_{1/2}$, V	$i_l t_p^{1/2}$, mA cm^{-2} s$^{1/2}$	$E_{1/2}$, V	$i_l t_p^{1/2}$, mA cm^{-2} s$^{1/2}$
50	−0.250	0.089	−0.375	0.070
100	−0.266	0.092	−0.365	0.073
250	−0.286	0.088	−0.348	0.070
500	−0.281	0.094	−0.335	0.073
1000	−0.303	0.097		
2000	−0.301	0.104		

[a] E_0(av) = −0.313 (±0.004) V calculated as $[(E_{1/2}(NP) + E_{1/2}(RP))/2]$.

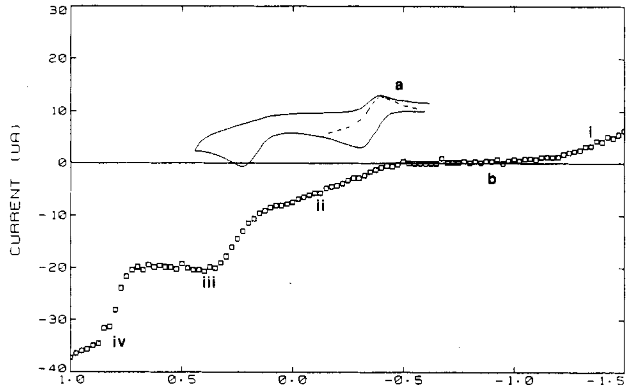

Figure 5. Electrochemistry of $Mo_2Cl_8^{4-}$ (no $MoCl_6^{3-}$ impurity) in basic $AlCl_3$–ImCl on GC: (a) cyclic voltammetry for $Mo_2Cl_8^{4-}$, v = 50 mV/s; (b) reverse-normal-pulse voltammetry for $Mo_2Cl_9^{3-}$, τ = 7 s at −1.65 V and t_p = 1000 ms. Voltammetric waves: (i) $Mo_2Cl_9^{3-}$ reduction to $Mo_2Cl_8^{4-}$; (ii) $Mo_2Cl_8^{4-}$ oxidation to $Mo_2Cl_8^{3-}$; (iii) $Mo_2Cl_8^{3-}$ oxidation to $Mo_2Cl_9^{3-}$; (iv) $Mo_2Cl_9^{3-}$ oxidation to $Mo_2Cl_9^{2-}$.

Normal-pulse and reverse-normal-pulse results for the first $Mo_2Cl_8^{4-}$ oxidation wave in the basic 0.8:1.0 melt are summarized in Table VIII. Despite the large separations in the $E_{1/2}$ values in the pulse experiments and in the E_p values in the cyclic experiments, an E_0 value of −0.313 V is calculated for both sets of experiments by simply averaging E_p^a and E_p^c for the cyclic results and $E_{1/2}$(NP) and $E_{1/2}$(RP) for the pulse results.

No detailed analyses of the second $Mo_2Cl_8^{4-}$ oxidation wave at ca. 0.3 V were performed. In the 0.8:1.0 melt discussed above, monomer impurities obscured this second oxidation wave. A $Mo_2Cl_8^{4-}$ solution free of monomer was prepared by adding ImCl to the 12 mM solution of $Mo_2Cl_9^{3-}$ in the slightly basic melt, producing a 0.8:1.0 melt, and then by performing electrolytic reduction at −1.7 V using a reticulated vitreous carbon (RVC) electrode. As discussed above, the monomer in this melt had been condensed to the dimer by manipulating the melt. From a cyclic voltammogram of $Mo_2Cl_8^{4-}$ recorded in this 0.8:1.0 basic melt where no monomer was present (Figure 5a), the relative height of this second oxidation indicates it to be a one-electron process. Scanning anodically of this second oxidation shows the appearance of a wave at 0.85 V corresponding to the oxidation of $Mo_2Cl_9^{3-}$. To confirm the formation of $Mo_2Cl_9^{3-}$, a reverse-normal-pulse experiment was performed. The potential was held at 0.6 V for 5 s to carry out the two one-electron oxidations of $Mo_2Cl_8^{4-}$, and then the potential was stepped cathodically. A large reduction wave at −1.4 V corresponding to the reduction of $Mo_2Cl_9^{3-}$ back to $Mo_2Cl_8^{4-}$ was observed.

A reverse-normal-pulse experiment was also performed on the monomer-free $Mo_2Cl_9^{3-}$ solution prior to the electrolysis at −1.7 V. The reverse-normal-pulse voltammogram shown in Figure 5b illustrates the interconversion of the two dimers. The experiment was performed by using the 0.8:1.0 melt made from addition of ImCl to the slightly basic melt originally 12 mM in $Mo_2Cl_9^{3-}$, i.e. the monomer-free melt discussed above prior to electrolysis at −1.7 V. The potential was held at −1.65 V for 7 s, and then the potential was stepped anodically. The cathodic wave at ca. −1.4 V is the "DC" wave and corresponds to the two-electron reduction of $Mo_2Cl_9^{3-}$ to $Mo_2Cl_8^{4-}$. Three reverse-pulse oxidation waves are observed. The first rather broad wave at −0.3 V is the initial one-electron oxidation of $Mo_2Cl_8^{4-}$ to $Mo_2Cl_8^{3-}$. The second wave at 0.3 V is the one-electron oxidation of $Mo_2Cl_8^{3-}$ to $Mo_2Cl_9^{3-}$, and the third wave at 0.8 V is the one-electron oxidation of $Mo_2Cl_9^{3-}$ to $Mo_2Cl_9^{2-}$. Relative heights of the currents agree with the number of electrons involved in each process, with eq 4 being used to compare the oxidation limiting currents to the reduction limiting current.

The first oxidation of $Mo_2Cl_8^{4-}$ probably does not involve large changes in the structure of the dimer since it is a quasi-reversible process. The one-electron-oxidized species may be formulated as $Mo_2Cl_8^{3-}$, and it is likely that an unbridged structure remains. After removal of the second electron, however, the δ bond is removed,[5] and the dimer rearranges to the bioctahedral structure of $Mo_2Cl_9^{3-}$ with bridging chlorides. This accounts for the irreversibility of the second oxidation process.

The potential for the first oxidation of $Mo_2Cl_8^{4-}$ relative to the reduction of $Mo_2Cl_9^{3-}$ is worthy of comment. It is apparent from the structures of these two dimers that significant electronic rearrangement must occur during their interconversion. The cathodic position of the $Mo_2Cl_9^{3-}$ reduction indicates that addition of electrons to its electronic structure is relatively difficult. By rearrangement to the $Mo_2Cl_8^{4-}$ structure and use of the added electrons to form Mo–Mo bonds, a more stable electronic arrangement is achieved, as demonstrated by the need to go to a potential considerably anodic of the reduction potential to begin removing these electrons.

Another point of interest is that this is the first time the initial oxidation of the $Mo_2Cl_8^{4-}$ anion has been observed. A previous assignment placed it nearer the second oxidation at 0.3 V; however, this oxidation was reported in aqueous HCl where the first oxidation would overlap the H^+/H_2 redox couple.[26] Other single-electron oxidations for quadruply bonded dimers without bridging ligands, specifically tetrachloro tetrakis(phosphine) dimers, have been reported in the literature.[27] The value of $E_{1/2}$ for the one-electron oxidation of $Mo_2Cl_4(PEt_3)_4$ is found to be 0.67 V in THF and 0.35 V in CH_2Cl_2 (vs. SCE), and similar values are observed for Mo(II) quadruply bonded dimers containing different phosphine ligands.[27] The potential of the SCE is at 0.24 V relative to the H^+/H_2 couple in aqueous solution. Therefore, from the potential of −0.45 V (vs. the reference electrode used in this study) for the H^+/H_2 couple in the basic 0.8:1.0 $AlCl_3$:ImCl melt,[11] the potential of the SCE can be approximated as −0.21 V relative to the reference electrode used in this study. On this basis, the oxidation of the $Mo_2Cl_8^{4-}$ anion is considerably more cathodic (at least 0.5 V more cathodic) than the oxidation of the neutral Mo(II) dimers containing phosphine ligands. The less anodic oxidation of the $Mo_2Cl_8^{4-}$ anion versus $Mo_2Cl_4(PR_3)_4$ is explained by the fact that phosphine ligands stabilize lower oxidation states, thus making it more difficult to oxidize $Mo_2Cl_4(PR_3)_4$ than $Mo_2Cl_8^{4-}$. This same trend is observed for reduction of $Re_2Cl_8^{2-}$ to $Re_2Cl_8^{3-}$ versus reduction of $Re_2Cl_4(PR_3)_4$ to $Re_2Cl_4(PR_3)_4^-$; the phosphine-containing Re(II) dimers are reduced at less cathodic (more anodic) potentials than $Re_2Cl_8^{2-}$.[5]

C. Electrochemistry of $Mo_2Cl_8H^{3-}$. A 16 mM solution of the hydride dimer was prepared by first adding the appropriate quantity of $K_4Mo_2Cl_8$ to a basic melt. As stated above, this salt was not soluble in the basic melt; however, after addition of $AlCl_3$, the $K_4Mo_2Cl_8$ reacted to produce a brown solid. Addition of enough ImCl to convert the acidic melt to an $AlCl_3$:ImCl molar ratio of 0.8:1.0 resulted in complete dissolution of the brown solid and produced a yellow-green solution. This procedure also ensured that no monomer impurities were present. The visible spectrum (see Figure 1 and Table I) indicated the solution contained the

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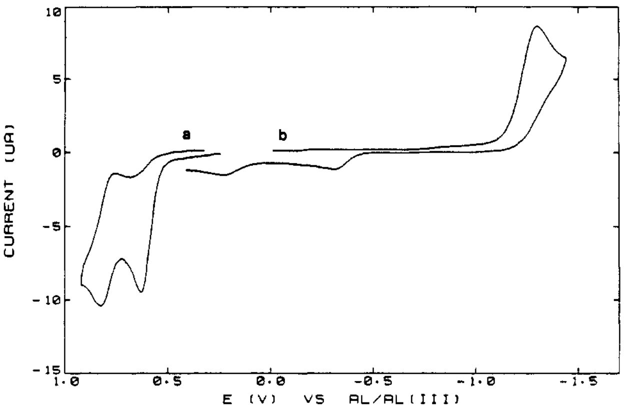

Figure 6. Cyclic voltammogram of 16 mM $Mo_2Cl_8H^{3-}$ in basic 0.8:1.0 $AlCl_3$:ImCl melt on GC (v = 5 mV/s). Initial scan direction: (a) anodic; (b) cathodic.

Table IX. Cyclic Voltammetric Parameters for Oxidation of 16 mM $Mo_2Cl_8H^{3-}$ in Basic 0.8:1.0 $AlCl_3$:ImCl Melt on Glassy Carbon

scan rate (v), mV/s	E_p^a, V	$E_p - E_{p/2}$, mV	$i_p^c/v^{1/2}$, mA cm^{-2} V$^{-1/2}$ s$^{1/2}$
5	0.625	50	1.69
50	0.655	60	1.37
100	0.671	65	1.34

hydride dimer, $Mo_2Cl_8H^{3-}$, almost exclusively.[25]

The cyclic voltammogram for $Mo_2Cl_8H^{3-}$ in Figure 6 shows a single reduction at ca. −1.3 V and two oxidations at 0.63 and 0.90 V. The two oxidation waves for $Mo_2Cl_8^{4-}$ are also apparent in the reverse scan following reduction of the hydride dimer.

(1) Oxidation of $Mo_2Cl_8H^{3-}$. The cyclic voltammetric parameters for the first oxidation wave at a GC electrode are summarized in Table IX. The large shift in the peak potential, E_p^a, with increasing scan rate and the $E_p - E_{p/2}$ values are consistent with an irreversible electron transfer at the faster scan rates.[15] The first oxidation was examined by reversing the scan before reaching the second oxidation and sweeping cathodically. When this was done, no reduction wave was seen for the product of the first oxidation, indicating this oxidation is accompanied by a following chemical reaction or structural rearrangement.

To examine the product of the first oxidation process, electrolysis using a RVC electrode was performed at 0.75 V. The visible spectrum showed the product to be $Mo_2Cl_9^{3-}$. The second oxidation wave seen in Figure 6 is the first oxidation of $Mo_2Cl_9^{3-}$. Since this $Mo_2Cl_9^{3-}$ oxidation has been shown to be a one-electron process, it was used to determine the number of electrons involved in the initial $Mo_2Cl_8H^{3-}$ oxidation. The $Mo_2Cl_9^{3-}$ oxidation was analyzed by holding the potential at 0.7 V for 10 s and then performing cyclic voltammetry. The $Mo_2Cl_9^{3-}$ oxidation peak current is described by eq 1. The peak current for the irreversible oxidation of $Mo_2Cl_8H^{3-}$ at ca. 0.65 V is described by[15]

$$i_p = (2.97 \times 10^5)n(\alpha n_a)^{1/2}ACD^{1/2}v^{1/2} \qquad (6)$$

at 22 °C, where α is the transfer coefficient, assumed to be 0.5, and n_a is the number of electrons involved in the rate-determining step and is assumed to be equal to n. This equation is valid since the data, although limited, indicate that the electron transfer is irreversible.[15] If the diffusion coefficients for $Mo_2Cl_8H^{3-}$ and $Mo_2Cl_9^{3-}$ are assumed to be the same, then n for the oxidation of $Mo_2Cl_8H^{3-}$ to form $Mo_2Cl_9^{3-}$ can be calculated by applying eq 1 and 6. At a scan rate of 100 mV/s, the n value for the first $Mo_2Cl_8H^{3-}$ oxidation is calculated to be 2.

Efforts to perform normal-pulse voltammetry on the oxidation region were hampered by the proximity of the two oxidations and the irreversible nature of the first oxidation, which caused it to shift toward the second reversible oxidation as the pulse width was shortened. At a pulse width of 1000 ms on a GC electrode, however, it was possible to distinguish both waves, and the ratio of the limiting current for the first oxidation to the limiting current for the second oxidation was ca. 2:1, consistent with the cyclic voltammetric results.

Table X. Cyclic Voltammetric Parameters for Reduction of 16 mM $Mo_2Cl_8H^{3-}$ in Basic 0.8:1.0 $AlCl_3$:ImCl Melt on Glassy Carbon

scan rate (v), mV/s	E_p^c, V	$E_p - E_{p/2}$, mV	$i_p^c/v^{1/2}$, mA cm^{-2} V$^{-1/2}$ s$^{1/2}$
5	-1.271	68	1.96
10	-1.288	70	2.01
20	-1.302	67	1.92
50	-1.316	66	1.87
100	-1.331	74	1.71
200	-1.348	78	1.59
500	-1.375		1.34

Reverse-normal-pulse experiments performed at a Pt electrode provided some evidence for the course of the first oxidation process. When the potential was held at 0.58 V for 5 s, thus carrying out only the first two-electron oxidation on $Mo_2Cl_8H^{3-}$, only the reverse current for proton reduction at ca. −0.4 V was observed.[11] The proton reduction limiting current observed for this reverse-normal-pulse experiment was nearly twice that seen for a normal-pulse experiment, which measured protonic impurities originally present in the melt. This indicates that the oxidation of $Mo_2Cl_8H^{3-}$ at 0.62 V results in the production of added protons.

From these results, the first oxidation can be postulated as

$$Mo_2Cl_8H^{3-} + Cl^- \rightarrow Mo_2Cl_9^{3-} + H^+ + 2e^- \qquad (7)$$

with the oxidation being viewed as conversion of a hydride ligand to a proton. Although the Mo's remain in their formal +3 oxidation state, the two-electron oxidation results in a loss of metal–metal interaction, as exemplified by the increase in Mo–Mo separation in solids from 2.38 Å for $Mo_2Cl_8H^{3-}$ to 2.6 Å for $Mo_2Cl_9^{3-}$. Also, considerable ligand rearrangement occurs.

(2) Reduction of $Mo_2Cl_8H^{3-}$. Results for the cyclic voltammetric study of this dimer on a glassy-carbon electrode are summarized in Table X. The peak potential shifts cathodically and the value of $i_p^c/v^{1/2}$ decreases with increasing scan rate. As with $Mo_2Cl_9^{3-}$, this indicates a complex reduction process. Comparison of the $i_p^c/v^{1/2}$ values for the reduction (Table X) to the $i_p^a/v^{1/2}$ values for the oxidation (Table IX) indicates that the reduction is probably a two-electron process. By the employment of electrolysis and visible spectroscopy, the product of the $Mo_2Cl_8H^{3-}$ reduction was identified as the quadruply bonded Mo(II) dimer $Mo_2Cl_8^{4-}$.

Normal-pulse voltammetry was also performed at the glassy-carbon electrode. The voltammograms, like those for $Mo_2Cl_9^{3-}$, were ill-defined at low scan rates; however, at longer pulse widths (≥500 ms), limiting plateaus were observed. No effort was made to determine a diffusion coefficient from the normal-pulse data, since it was limited to too short a pulse width range.

Reverse-normal-pulse experiments were performed on the reduction process at a Pt electrode to search for the production of H_2 during the $Mo_2Cl_8H^{3-}$ reduction. The experiments were complicated by reduction of proton impurities in the melt to H_2 and by overlap of the $Mo_2Cl_8^{4-}$ oxidation wave with the H_2 oxidation wave. Qualitatively, however, it appeared that more H_2 was produced during the dimer reduction than was seen when only the protonic impurities were reduced by using a less cathodic generation potential. The reduction process is postulated to be that in eq 8. The proton on the left may be a protonic impurity.

$$Mo_2Cl_8H^{3-} + 2e^- + H^+ \rightarrow Mo_2Cl_8^{4-} + H_2 \qquad (8)$$

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