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Molybdenum(II) Chloride in the Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Molten Salt. Electrochemical and Spectroscopic Characterization of the $[(Mo_6Cl_8)Cl_6]^{2-}$ Ion in Neutral and Basic Melts

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Absorption spectroscopy and titration experiments suggest that molybdenum(II) chloride is complexed as the hexanuclear $[(Mo_6Cl_8)Cl_6]^{2-}$ cluster in the basic and the neutral–basic aluminum chloride–1-methyl-3-ethylimidazolium chloride molten salt. Only a single voltammetric reduction wave at $E_p^c = \sim 1.23$ V versus aluminum in the 66.7/33.3 mol % melt can be seen for this complex at a glassy carbon electrode in basic melt, but the reduction product is not stable. However, if all of the unbound chloride ion in basic melt containing $[(Mo_6Cl_8)Cl_6]^{2-}$ is carefully removed by titration with acidic melt, it is possible to also observe a reversible one-electron oxidation wave with $E_{1/2}$ = 1.55 V corresponding to the oxidation of this complex to $[(Mo_6Cl_8)Cl_6]^-$. This species is stable on the voltammetric time scale, but attempts to produce bulk solutions of this oxidant were unsuccessful because it is slowly reduced by some component of the neutral melt. The $[(Mo_6Cl_8)Cl_6]^{2-}$ complex luminesces in basic melt with an emission maximum centered at ca. 700 nm (uncorrected) when irradiated at 400 nm. Molybdenum(II) is very soluble in moderately acidic melt (>55 mol % $AlCl_3$), but it is not electroactive. However, it luminesces in this melt at 710 nm (uncorrected) when irradiated at 400 nm, suggesting that the $(Mo_6Cl_8)^{4+}$ core is retained after dissolution.

Introduction

Room-temperature chloroaluminate ionic liquids are obtained when aluminum chloride is combined with certain quaternary ammonium chloride salts, notably 1-(1-butyl)pyridinium chloride (BupyCl) and 1-methyl-3-ethylimidazolium chloride (MeEtimCl).[1] The Lewis acid–base properties of these molten salts are dependent upon the molar ratio of the aluminum chloride to the organic salt. Anhydrous mixtures prepared with an excess of the former component are "acidic" because they contain chloride ion accepting species like $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$, and mixtures prepared with an excess of the latter are "basic" because they contain chloride ion that is not covalently bound to aluminum. "Neutral" melts are obtained when the molar ratio of the two components is exactly 1. Such melts are composed principally of organic cations (R^+) and $AlCl_4^-$ and small quantities of $Al_2Cl_7^-$ and Cl^- that arise from the autoionization reaction

$$2R^+AlCl_4^- \rightleftharpoons R^+Al_2Cl_7^- + R^+Cl^- \qquad (1)$$

The equilibrium constant for this reaction is believed to be in the vicinity of 10^{-16}–10^{-17} at 40 °C.[2] It has been reported that neutral $AlCl_3$–MeEtimCl melts exhibit an electrochemical window of approximately 4.4 V, which is roughly a combination of the negative potential limit of the basic melt and the positive potential limit of the acidic melt.[3]

Room-temperature chloroaluminate molten salts have proven to be very useful solvents for stabilizing both monomeric and polymeric transition-metal chloride complexes.[4] In many cases, they have been shown to be superior to molecular solvents like water and acetonitrile because the solvation and solvolysis pathways that are often available to these complexes in molecular solvents are absent in the melts.[4,5] However, one major disadvantage of these molten salts is their extraordinary sensitivity to moisture; this property necessitates that they and their components be handled only in a glove box with an inert atmosphere.

Several investigations that were concerned with the electrochemistry of molybdenum solutes in chloroaluminate molten salts have appeared in the literature. Marshall and Yntema[6] examined the electrolytic reduction of both MoO_3 and $K_3[MoCl_6]$ in the $AlCl_3$–NaCl–KCl (66/20/14 mol %) melt and obtained a "spongy" black deposit believed to be molybdenum metal. However, these results have been questioned by others.[7] Phillips and Osteryoung[8] conducted an extensive study involving several molybdenum chloride and oxide chloride compounds in the $AlCl_3$–NaCl (50/50 mol %) melt at 175 °C. Molybdenum(V) and molybdenum(III) species were stable in this melt, but added molybdenum(VI) was spontaneously reduced by the melt to molybdenum(V). The voltammetric reduction of the latter to the metal at a glassy carbon electrode was found to proceed by a complicated mechanism involving two intermediate molybdenum(III) species and two different molybdenum(II) electrode surface deposits. $[MoCl_6]^{2-}$ was found to be stable in the basic $AlCl_3$–MeEtimCl melt and to undergo a reversible reduction to the corresponding molybdenum(III) hexachloride species at a glassy carbon electrode.[9] The voltammetric half-wave potential, $E_{1/2}$, of the $[MoCl_6]^{2-/3-}$ electrode process was estimated to be 0.174 V versus aluminum in the 66.7/33.3 mol % melt. Carlin and Osteryoung[10] investigated the electrochemistry of the dimeric molybdenum(III) complexes $[Mo_2Cl_9]^{3-}$ and $[Mo_2Cl_8H]^{3-}$ and the dimeric metal–metal-bonded molybdenum(II) complex $[Mo_2Cl_8]^{4-}$ in this same melt. The latter species can be oxidized voltammetrically to $[Mo_2Cl_8]^{3-}$ at a glassy carbon electrode in a one-electron quasireversible reaction with $E_{1/2}$ = –0.313 V versus aluminum in the 60/40 mol % melt. In turn, this species can be oxidized to $[Mo_2Cl_9]^{3-}$. The hydride complex undergoes a two-electron oxidation reaction to yield this same complex and a proton. The voltammetric oxidation peak potential for this process is approximately 0.63 V at slow scan rates. A two-electron reduction wave corresponding to the conversion of $[Mo_2Cl_9]^{3-}$ to $[Mo_2Cl_8]^{4-}$ was also observed.

The reduction of $MoCl_5$ with aluminum metal in $AlCl_3$–NaCl is a facile synthetic route to octahedral, metal–metal-bonded species based on the hexanuclear molybdenum(II) cluster unit $(Mo_6Cl_8)^{4+}$.[11] Each molybdenum atom of this cluster unit is joined to four others through formal single bonds with Mo–Mo distances of ca. 0.26 nm.[12] Thus, like the molybdenum atoms

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Table I. Addition of Molybdenum(II) Chloride to "Neutral-Basic" $AlCl_3$–MeEtimCl

$10^4 n_{Cl}{}^0$	$10^5 n_{Mo}{}^0$	$10^4 n_{Cl}{}^f$	$n_{Mo}{}^0/(n_{Cl}{}^0 - n_{Cl}{}^f)$
3.59	1.24	3.34	2.01
3.01	2.67	2.50	1.91
5.18	3.20	4.59	1.84
			av: 1.92 ± 0.09

in the well-known quadruply bonded molybdenum(II) chloride complex $[Mo_2Cl_8]^{4-}$, each molybdenum atom in this species participates in four metal–metal bonds. Although compounds containing the $(Mo_6Cl_8)^{4+}$ cluster unit have been synthesized in molten chloroaluminates, there is a paucity of information about the electrochemistry of such species in molten salts. In this article, we present the results of an electrochemical and spectroscopic study of molybdenum(II) chloride, $(Mo_6Cl_8)Cl_4$, in neutral and basic $AlCl_3$–MeEtimCl melts.

Experimental Section

Apparatus. Electrochemical measurements were conducted inside a nitrogen-filled Kewaunee Scientific Equipment Corp. (KSE) glovebox that was equipped with a KSE Model 2C2500 30 ft^3 min^{-1} inert-gas purifier. The moisture and oxygen content of the glovebox atmosphere were monitored by observing the lifetime of the exposed filament of a 25-W incandescent light bulb.[13] Cyclic and rotating disk electrode voltammetry and bulk controlled-potential electrolysis were performed with an EG & G Princeton Applied Research Corp. Model 173 potentiostat, which was equipped with a PARC Model 179 digital coulometer plug-in module. A PARC Model 175 universal programmer was used to provide voltammetric waveforms. Electrochemical data were displayed on a Houston Instruments Model 100 X-Y/Y-t recorder or a Nicolet Explorer I digital oscilloscope. Electronic resistance compensation was applied during all experiments except controlled-potential electrolysis. The glassy carbon rotating disk electrode (geometrical area = 0.071 cm^2), the counter and reference electrodes, the electrochemical cell, and the furnace used to heat the cell were identical with those used in a previous study.[14] Bulk electrolysis experiments were performed in a glassy-carbon cup or alternately in a small Pyrex cell with a large surface area platinum-basket working electrode. Spectroelectrochemical experiments were carried out directly in the glovebox by using the microprocessor-controlled, fiber-optic-based spectroelectrochemistry system and a cell with a reticulated glassy-carbon, optically transparent electrode (RGC-OTE) described in previous articles.[15] All potentials are reported versus aluminum immersed in the nominal 66.7/33.3 mol % $AlCl_3$–MeEtimCl melt.

Absorption spectra were recorded outside the glovebox in 1 mm path length fused silica cells by using either a CARY Model 2290 or a Perkin-Elmer Model 3840 Lambda Array UV–vis spectrophotometer. Luminescence measurements were made in standard four-sided, 1 cm path length fused silica cells by using a Perkin-Elmer Model LS-5B luminescence spectrometer. Both the absorption and luminescence cells were fitted with airtight Teflon caps.

Chemicals. The purification of $AlCl_3$ by vacuum sublimation, the synthesis and recrystallization of MeEtimCl, and the preparation of the $AlCl_3$–MeEtimCl molten salt have been described.[16] Molybdenum(II) chloride, $(Mo_6Cl_8)Cl_4$ (Cerac, 99.5 %), was used as received.

Results and Discussion

Titration Experiments. Osteryoung and co-workers[17] demonstrated that it is sometimes possible to determine the number of chloride ions taken up by a species or complexed during dissolution in "neutral–basic"[18] melt by monitoring the decrease in the chloride ion voltammetric oxidation current, which is directly proportional to the chloride ion concentration in the melt. This "amperometric" titration technique works best when the resulting complex does not undergo oxidation at potentials proximate to the addition of chloride ion. We conducted titration experiments with molybdenum(II) chloride by adding a small amount of this compound to a fixed volume of 50/50 mol % melt containing an excess of MeEtimCl relative to the number of moles of $(Mo_6Cl_8)Cl_4$ to be added. The chloride ion oxidation current, which can be seen at ca. $E_p{}^a$ = 1.1 V at a glassy-carbon electrode in this melt, was recorded before and after the addition of the molybdenum(II) chloride. It was necessary to carry out these experiments at 90 °C in order to ensure sufficient solubility of the added $(Mo_6Cl_8)Cl_4$ in the nominal 50.0/50.0 mol % melt. Fortunately, subsequent voltammetric experiments revealed that the chloride complex of molybdenum(II) produced in these experiments was quite stable in the melt at this temperature. The results of three such experiments are recorded in Table II; $n_{Cl}{}^0$, $n_{Mo}{}^0$, and $n_{Cl}{}^f$ represent the number of moles of chloride ion in the melt before the addition of the molybdenum(II) chloride, the moles of molybdenum(II) chloride added as $(Mo_6Cl_8)Cl_4$, and the number of moles of chloride ion remaining in the melt after the dissolution of $n_{Mo}{}^0$ moles of $(Mo_6Cl_8)Cl_4$, respectively. The ratio $n_{Mo}{}^0/(n_{Cl}{}^0 - n_{Cl}{}^f)$ reflects the number of moles of chloride ion that are taken up per mole of $(Mo_6Cl_8)Cl_4$ during the dissolution process. The average value of this ratio, 1.9 ± 0.1, clearly indicates that two chloride ions are taken up per $(Mo_6Cl_8)Cl_4$ unit during the dissolution process according to the reaction

$$(Mo_6Cl_8)Cl_4 + 2Cl^- \rightarrow [(Mo_6Cl_8)Cl_6]^{2-} \qquad (2)$$

Similar titration experiments were attempted in the 50.0/50.0 mol % melt containing a slight excess of $AlCl_3$ in an attempt to determine the number of chloride ions, if any, given up by the molybdenum(II) chloride upon dissolution in acidic melt. Unfortunately, these experiments were thwarted by the almost complete insolubility of this compound in this melt (vide infra).

Table II. Absorption Spectroscopic Data for Molybdenum(II) Chloride in Various Solvents

solvent	λ, nm (ε, M^{-1} cm^{-1})	ref
5 M aqueous HCl	307 (2.9 × 10^3), 345[a] (2.7 × 10^3)	19
12 M aqueous HCl	304 (2.7 × 10^3), 344[a] (2.3 × 10^3)	this work
44.4/55.6 mol % $AlCl_3$–MeEtimCl	313 (4.0 × 10^3), 353[a] (3.5 × 10^3)	this work
55.0/45.0 mol % $AlCl_3$–MeEtimCl	304[a] (3.2 × 10^3), 342,[a] 425[a]	this work

[a] Shoulder.

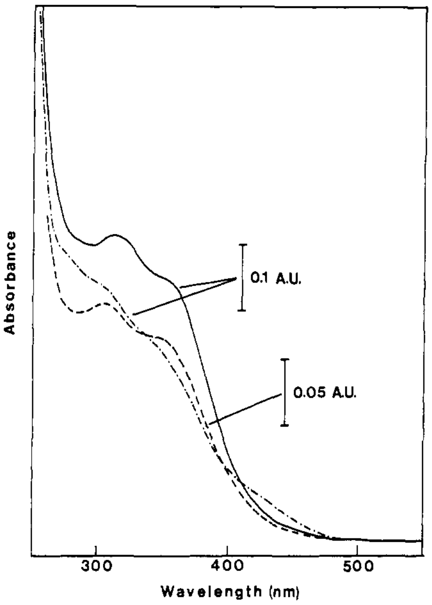

Figure 1. Absorption spectra of $(Mo_6Cl_8)Cl_4$ in various solvents at room temperature: (—) 1.13 × 10^{-3} M in 44.4/55.6 mol % $AlCl_3$–MeEtimCl melt; (– –) 6.4 × 10^{-4} M in 12 M aqueous HCl; (–·) 1.19 × 10^{-3} M in 55.0/45.0 mol % $AlCl_3$–MeEtimCl melt. The cell path lengths were 1.00 mm.

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(18) "Neutral-basic" melt is 50.0/50.0 mol % $AlCl_3$–BupyCl or $AlCl_3$–MeEtimCl containing a slight excess of BupyCl or MeEtimCl, respectively.

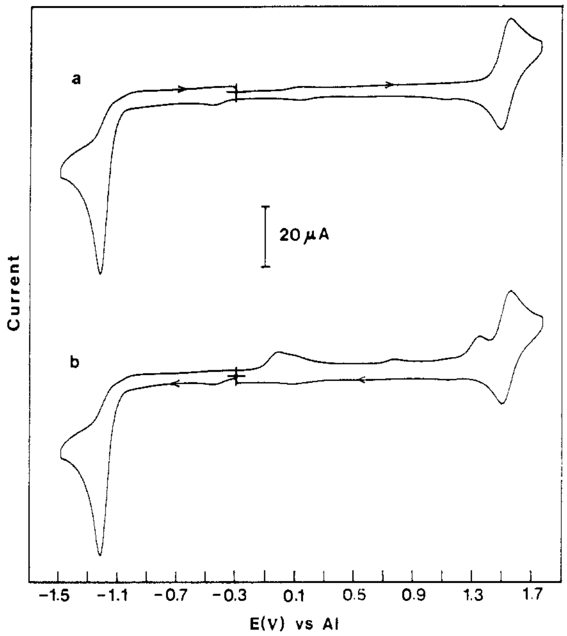

Figure 2. Cyclic voltammograms of 5.34×10^{-3} M $[(Mo_6Cl_8)Cl_6]^{2-}$ in 50.0/50.0 mol % $AlCl_3$–MeEtimCl melt at a glassy carbon electrode at 53 °C: (a) positive sweep; (b) negative sweep. The scan rates were 100 mV s^{-1}, and the initial potential for each scan was −0.30 V.

Absorption Spectra. Molybdenum(II) chloride, $(Mo_6Cl_8)Cl_4$, dissolved in basic and moderately acidic $AlCl_3$–MeEtimCl melt to produce yellow solutions. An absorption spectrum of a solution prepared with 44.4/55.6 mol % melt is shown in Figure 1 along with an absorption spectrum of molybdenum(II) chloride in aqueous HCl, where this compound is known to be complexed as $[(Mo_6Cl_8)Cl_6]^{2-}$.[19,20] Wavelength and absorptivity data that were taken from the spectra in this figure are collected in Table I. The overall appearances of these two spectra are very similar, and the positions of their absorption bands are in good agreement, confirming that molybdenum(II) is complexed as $[(Mo_6Cl_8)Cl_6]^{2-}$ in basic $AlCl_3$-MeEtimCl. A spectrum of molybdenum(II) recorded in the 55.0/45.0 mol % melt is also shown in Figure 1. This spectrum consists only of poorly defined shoulders at ca. 304, 342, and 425 nm; however, note that the 304- and 342-nm shoulders appear at approximately the same wavelengths as do the absorption bands in the spectrum recorded in basic melt.

Electrochemistry of $[(Mo_6Cl_8)Cl_6]^{2-}$. Solutions of $[(Mo_6Cl_8)Cl_6]^{2-}$ in basic melt exhibit only a single voltammetric reduction wave with $E_p^c = -1.23$ V at a glassy-carbon electrode. No oxidation wave could be seen for $[(Mo_6Cl_8)Cl_6]^{2-}$ prior to the oxidation of unbound chloride ion, which is the positive limit of the basic melt. However, when sufficient acidic melt was added to basic melt containing $[(Mo_6Cl_8)Cl_6]^{2-}$ so as to reduce the free chloride ion concentration in this melt to virtually zero, i.e., when the basic melt was made exactly neutral, it was possible to observe *both* oxidation and reduction waves for this complex. Figure 2 shows voltammetric scans at a glassy-carbon electrode for a solution of $[(Mo_6Cl_8)Cl_6]^{2-}$in the 50.0/50.0 mol % melt that were initiated in the positive and negative directions. An oxidation wave at 1.53 V and an associated reduction wave at 1.47 V can be seen in this melt in addition to the reduction wave described above. When the negative scan (Figure 2b) is reversed immediately after the reduction wave at −1.23 V is traversed, small oxidation waves can be seen at −0.04, 0.75, and 1.32 V. These waves obviously arise from species produced during the decomposition of the $[(Mo_6Cl_8)Cl_6]^{2-}$ reduction product. Since this reduction process appears to lead to complete destruction of the cluster, we did not investigate it further.

Some typical cyclic voltammetry data for the oxidation process with $E_p^a = 1.53$ V are given in Table III. For this wave, ΔE_p and $E_p^a - E_{1/2}$ are 0.062 and 0.031 V, respectively, at the slowest scan rate that was examined, 0.010 V s^{-1}. These values are in very good agreement with the theoretical values of 0.064 and 0.031 V expected for a one-electron, reversible electrode reaction at 52 °C. Both ΔE_p and $E_p^a - E_{1/2}$ exhibit only a very modest increase with increasing scan rate. There also seems to be a small negative shift in the E_p^a values recorded in this table; however, this shift is less than the uncertainty in these measurements, which is typically ±10 mV. The peak current ratio, i_p^c/i_p^a, estimated by using Nicholson's empirical procedure,[21] is very close to 1.0, and the peak current function, $i_p^a/v^{1/2}$, is essentially constant over the range of scan rates that were investigated. This oxidation process was also investigated with rotating disk electrode (RDE) voltammetry; a plot of the limiting current, i_l, for the oxidation of $[(Mo_6Cl_8)Cl_6]^{2-}$ versus the square root of the angular velocity of the RDE was linear and passed through the origin. A plot of E versus $\log[(i_l - i)/i]$, constructed from data taken from the descending portion of a typical RDE voltammogram for the oxidation of $[(Mo_6Cl_8)Cl_6]^{2-}$, was linear and gave a value of $n = 0.9$. Taken together, the results presented above suggest that this oxidation process corresponds to the reaction

$$[(Mo_6Cl_8)Cl_6]^{2-} \rightleftharpoons [(Mo_6Cl_8)Cl_6]^{-} + e^{-} \qquad (3)$$

in which the product is stable on the voltammetric time scale. A series of multiple-sweep cyclic voltammograms that covered the potential range from 0 to 1.80 V supported this conclusion, since no new voltammetric waves, including that for the oxidation of unbound chloride ion, appeared in the melt during these scans.

Table III. Cyclic Voltammetric Data for the Oxidation of $[(Mo_6Cl_8)_6]^{2-}$ in 50.0/50.0 mol % $AlCl_3$–MeEtimCl at 52 °C

v, V s^{-1}	E_p^a, V	$E_{1/2}$,[a] V	ΔE_p, V	i_p^c/i_p^a	$10^4 i_p^a/v^{1/2}$, A $s^{1/2}$ $V^{-1/2}$
0.010	1.533	1.564	0.062	1.00	1.12
0.020	1.530	1.563	0.065	0.97	1.16
0.050	1.532	1.566	0.068	1.13	1.14
0.100	1.525	1.560	0.070	1.03	1.15
0.200	1.525	1.560	0.070	1.07	1.14

[a] Estimated from the voltammetric peak potentials by using $(E_p^c + E_p^a)/2$.

Controlled-potential electrolysis experiments were performed at an applied potential of 1.80 V both in a glassy carbon cup and in a Pyrex cell with a large surface area platinum-basket working electrode in order to see if it was possible to prepare a stable bulk solution of the $[(Mo_6Cl_8)Cl_6]^{2-}$ oxidation product. During these experiments, the melt changed from an initial yellow color to orange; however, the electrolysis current decreased only slightly from its initial value and reached a steady-state value as the experiment progressed. Analysis of the [Ox]/[Red] ratios in these solutions with RDE voltammetry indicated that only ca. 15–20% of the original complex was oxidized at this point. If the potential applied to the working electrode of the electrolysis cell was discontinued, the rest potential of this electrode drifted in a negative direction, and the solution reverted to its original yellow color within a few hours. Alternately, the yellow color could be restored immediately by adding one or two drops of basic melt to the electrolyzed solution. If the electrolysis experiment was continued for an extended period of time so that the total charge passed was in substantial excess of that required for a one-electron oxidation of all of the $[(Mo_6Cl_8)Cl_6]^{2-}$, then the solution became orange-brown and a precipitate of unknown composition began to form. However, after standing overnight, this solution returned to its initial yellow color and the precipitate dissolved.

Similar controlled-potential electrolysis experiments were conducted with a cell containing an RGC-OTE. By using this cell and associated equipment, it was possible to electrolytically generate a substantial steady-state concentration of the $[(Mo_6Cl_8)Cl_6]^{2-}$ oxidation product and to then record the visible absorption spectrum of this species. Spectra obtained in this

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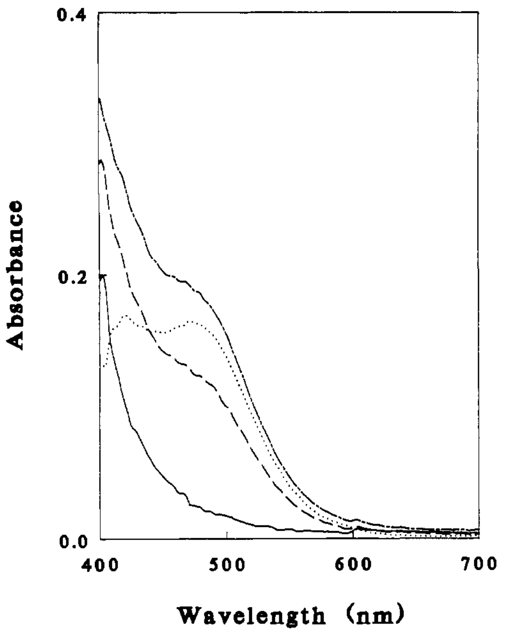

Figure 3. Visible absorption spectra recorded in the RGC-OTE cell at 40 °C during the controlled-potential oxidation of a 1.97×10^{-3} M solution of $[(Mo_6Cl_8)Cl_6]^{2-}$ in 50.0/50.0 mol % $AlCl_3$–MeEtimCl at an applied potential of 1.80 V: (—) background spectrum before electrolysis commenced; (– –) spectrum at some intermediate time during the electrolysis; (–·) spectrum after steady-state conditions were achieved; (···) difference between the latter spectrum and the background spectrum.

manner are depicted in Figure 3, and they clearly show the emergence of an absorption band at ca. 480 nm and, less equivocally, a very weak shoulder at 420 nm as the electrolysis progresses. The latter is more apparent after the background spectrum is subtracted from the steady-state spectrum. Bands were reported at these same positions for dichloromethane solutions containing electrolytically generated $[(Mo_6Cl_8)Cl_6]^-$.[22]

$[(Mo_6Cl_8)Cl_6]^-$ is known to be a very powerful oxidant,[22] and we suspect that it reacts with some component of the melt as it is produced during electrolysis, reaching a steady-state concentration that is dictated by its rate of reduction. These results are unanticipated since $E_{1/2}$ for the $[(Mo_6Cl_8)Cl_6]^{-/2-}$ couple (1.55 V) appears to be well within the positive potential limit of the neutral melt, which is generally considered to be ca. 2.0 V. However, this positive limit is based on voltammetric observations and may actually be a "kinetic artifact" because a rough calculation of the formal potential of the chlorine redox couple in neutral melt yields a value of only 1.37 V versus aluminum in the 66.7/33.3 mol % melt.[23] Thus, the equilibrium potential of the chlorine redox couple should be in the vicinity of this value.

Table IV. Summary of Electrochemical Data for $[(Mo_6Cl_8)_6]^{2-}$ in 50.0/50.0 mol % $AlCl_3$–MeEtimCl at 52 °C

$E_{1/2}$,[a] V	$E_{1/2}$,[b] V	$10^7 D$,[a] cm^2 s	$10^7 D$,[b] cm^2 s	$10^{10}\eta D/T$,[c] g cm s^{-2} K^{-1}
1.55 ± 0.1	1.55 ± 0.1	4.9 ± 0.3	6.2 ± 0.5	1.6 ± 0.1

[a] Cyclic voltammetry. [b] Rotating disk electrode voltammetry. [c] Average value calculated from cyclic and rotating disk electrode voltammetry.

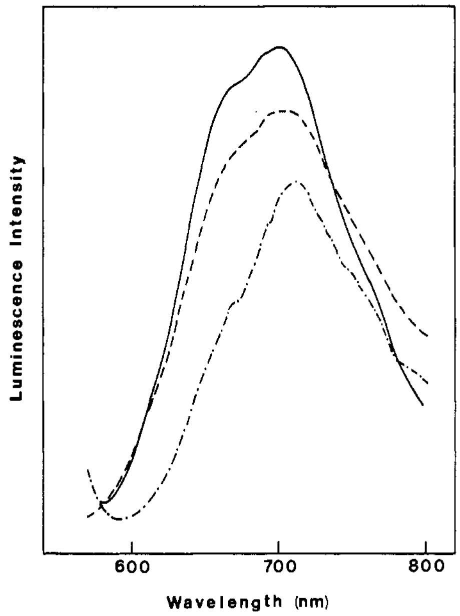

Figure 4. Uncorrected emission spectra (arbitrary units) of molybdenum(II) chloride at room temperature: (—) 1.0×10^{-3} M in 44.4/55.6 mol % $AlCl_3$–MeEtimCl melt (excitation at 400 nm); (– –) 6.4×10^{-4} M in 12 M aqueous HCl (excitation at 420 nm); (–·) 1.19×10^{-3} M in 55.0/45.0 mol % $AlCl_3$–MeEtimCl (excitation at 400 nm).

If neutral melt containing $[(Mo_6Cl_8)Cl_6]^{2-}$ was made slightly acidic by the addition of acidic melt, then virtually all of the molybdenum(II) precipitated; however, this precipitate began to dissolve as the melt was made progressively more acidic. In fact, molybdenum(II) chloride dissolves easily in moderately acidic melt (≥55 mol % $AlCl_3$) with heating and stirring. Unfortunately, no oxidation or reduction waves attributable to molybdenum(II) could be detected in these solutions, suggesting that this species is not electroactive within the electrochemical window of acidic melt.

Diffusion Coefficients. Diffusion coefficients, *D*, for $[(Mo_6Cl_8)Cl_6]^{2-}$ that were determined by using cyclic and RDE voltammetry are shown in Table IV. Also included in this table is the Stokes–Einstein product, $\eta D/T$, where η is the absolute viscosity of the melt and *T* is the absolute temperature. This product is inversely proportional to the radius of the diffusing species. The magnitude of $\eta D/T$ for complex ions in these melts has been shown to depend strongly upon the overall charge on the complex.[25] This dependence appears to arise from interactions between the charged species and cations in the melt during the diffusion process. In fact, the cations that are associated with the complex appear to be more important in determining the size of the diffusing entity than the size of the "bare" complex because it appears unimportant whether the complex is monomeric or polymeric; e.g., $[Re_3Cl_{12}]^{3-}$ exhibits the same $\eta D/T$ value as $[IrCl_6]^{3-}$.[25] The value of $\eta D/T$ found here for $[(Mo_6Cl_8)Cl_6]^{2-}$ is significantly smaller than that for other ions with the same overall charge and thus appears to depart from this trend. Perhaps in the present case the hexanuclear complex without associated cations is itself large enough to contribute significantly to the size of the diffusing entity.

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(23) Karpinski and Osteryoung[24] represent the chlorine redox couple in the basic $AlCl_3$–BupyCl and $AlCl_3$–MeEtimCl molten salts as $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ with $E^{\circ\prime} = 0.251$ V versus $Ag^+(0.01\ M)/Ag$ in the 60.0/40.0 mol % $AlCl_3$–MeEtimCl melt. Likewise, the chlorine redox couple in acidic $AlCl_3$–BupyCl melt is given by these authors as $Cl_2 + 2Al_2Cl_7^- + 2e^- \rightleftharpoons 4AlCl_4^-$ with $E^{\circ\prime} = 1.302$ V versus $Ag^+(0.01\ M)/Ag$. (In practice, chlorine reacts with $MeEtim^+$ in acidic $AlCl_3$–MeEtimCl melt, and so the value measured in $AlCl_3$–BupyCl must be used as an estimate of the chlorine redox couple in the former solvent.) The chlorine redox couple in exactly neutral $AlCl_3$–MeEtimCl melt should be the combination of these two reactions: $Cl_2 + Al_2Cl_7^- + 2e^- \rightleftharpoons Cl^- + 2AlCl_4^-$ with an $E^{\circ\prime}$ of about 0.777 V versus $Ag^+(0.01\ M)/Ag$. The potential of the $Ag^+(0.01\ M)/Ag$ reference electrode is reported to be +0.590 V versus an Al electrode immersed in the 66.7/33.3 mol % $AlCl_3$–BupyCl melt.[24] If we assume that the $Ag^+(0.01\ M)/Ag$ redox couple exhibits nearly the same potential in the $AlCl_3$–MeEtimCl melt system, then $E^{\circ\prime}$ for the chlorine electrode in this melt should be in the vicinity of ca. 1.37 V versus the reference electrode used in the present study. The potential required for the oxidation of chloride ion and chloride-containing species in these melts appears to depend strongly upon the electrode material that is used,[24] providing further support for the kinetic nature of the reported electrochemical window of neutral melt.

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Luminescence Spectra. The $[(Mo_6Cl_8)Cl_6]^{2-}$ ion has been shown to exhibit metal-centered luminescence near 700 nm in various solvents.[22,26] It was of great interest to see if similar emission could be detected in the $AlCl_3$–MeEtimCl melt because molten salts have rarely been used for such measurements. We found that the melt exhibits luminescence near 480 nm (uncorrected) when irradiated at wavelengths shorter than ca. 400 nm. The intensity of this luminescence could be decreased substantially, but not eliminated entirely, by treating the MeEtimCl with activated charcoal several times during the recrystallization process, suggesting that this luminescence originated from an impurity associated with the MeEtimCl. However, if solutions of $[(Mo_6Cl_8)Cl_6]^{2-}$ in 50/50 mol % melt were irradiated at exactly 400 nm, it was possible to observe an emission band centered at λ_{max} = 700 nm (uncorrected) that was very similar to that seen for this ion in nitrogen-saturated aqueous HCl (Figure 4). In addition, it was found that solutions of molybdenum(II) in the 55.0/45.0 mol % melt also luminesce at λ_{max} = 710 nm (uncorrected) (Figure 4), suggesting that the $(Mo_6Cl_8)^{2+}$ core may be preserved when molybdenum(II) is dissolved in acidic melt. However, the identity of the extant species in acidic melt could not be determined with the techniques available to us. In conclusion, these results indicate that the $AlCl_3$–MeEtimCl molten salt may be of modest value for luminescence measurements, provided that excitation of the melt or of the seemingly inescapable impurities in the melt is avoided.

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Crystal Structures and Single-Crystal Optical Absorption Spectra for Two New Polymorphs of Tetrakis(μ-pivalato)dimolybdenum(II)[1]

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Two new polymorphs, β- and γ-$Mo_2[O_2CC(CH_3)_3]_4$, were crystallized. The crystal structure of the β-form indicates an *I*2/*c* unit cell with *a*–*c* = 12.747 (3), 18.322 (3), and 11.369 (1) Å, β = 91.83 (1)°, and *Z* = 4. The crystal structure of the γ-form indicates a *Pbcn* unit cell with *a*–*c* = 12.711 (3), 18.351 (5), and 11.413 (3) Å and *Z* = 4. Both structures have one-dimensional chains of molecules formed by weak two Mo⋯O bonds between adjacent molecules, a common feature of many dimolybdenum tetracarboxylates. There is some indication of disorder of the methyl carbons in the tertiary butyl groups on the chelate rings not involved in intermolecular bonding. Single-crystal polarized absorption spectra are presented for the $1\bar{1}0$ face for the β-form and the 110 face for the γ-form. The spectra of both forms possess highly resolved vibrational structure. In the β-form the spectra indicate three different sites with origins at 21 875, 21 900, and 21 950 cm^{-1}, and in the γ-form there are two different sites with origins at 21 925 and 21 985 cm^{-1}. The spectra indicate that this first absorption band for each form is a weak nondegenerate electric dipole allowed transition with comparable intensities arising from vibronic contributions of degenerate molecular vibrations. They are therefore assigned as the $\delta \rightarrow \delta^*$ transition. There is evidence that the transition moment vectors have been shifted significantly away from the Mo–Mo bond direction. Long Frank–Condon progressions provide information about vibrational frequencies in the excited state.

Introduction

X-ray diffraction crystal structure determinations for a number of dimolybdenum tetracarboxylates[2-4] have shown that the molecules normally stack in one-dimensional chains with pairs of weak intermolecular Mo⋯O bonds between adjacent molecules, as is illustrated in Figure 1. The asymmetry introduced by this intermolecular bonding in the crystal packing has a profound effect on the optical absorption spectra of the crystals of these compounds.[5-7] The dimeric molecules possess an approximate local D_{4h} symmetry out through the bond to the R group in Figure 1. The first observed absorption band in the spectra is considered to correspond to the spin-allowed $\delta \rightarrow \delta^*$ transition, ($^1A_{1g} \rightarrow {}^1A_{2u}$; $b_{2g} \rightarrow b_{1u}$). Such a molecular transition is electric dipole allowed with *z* polarization, i.e., with the transition moment directed along the metal–metal bond, which is the 4-fold symmetry axis. The transitions are weak, however, presumably because their intensity is dependent upon the small interatomic overlap of the δ orbitals on the separate metal atoms. The spectra for these compounds have rich vibrational structure; long Franck–Condon progressions, based on the Mo–Mo stretching frequency, have been observed on a number of vibronic origins as well as the O–O line. The polarization ratio for the O–O line in the acetate for two different faces[5] indicated that the transition-moment vector for the $\delta \rightarrow \delta^*$ transition did not lie along the metal–metal bond but was oriented 32° away from the bond and was approximately in the plane containing the intermolecular Mo⋯O bonds. Polarization ratios for other carboxylates have also indicated an appreciable deviation of the transition moment vectors away from the metal–metal bond.

Very recently, Cotton and Zhong[8] reported the spectra for $Mo_2[O_2CC(C_6H_5)_3]_4 \cdot 3CH_2Cl_2$. This crystal has a tetragonal lattice with the metal–metal bond aligned with the crystallographic *c* axis, and there was no intermolecular bonding. The spectra indicated multiple sites that were dependent on the loss of CH_2Cl_2 molecules. However, origin lines were *c* and therefore *z* polarized while a number of vibronically excited lines had *a* and therefore *x*,*y* polarization. These results together with the pattern of hot bands observed are also consistent with an assignment of the first absorption band as a weak electric dipole allowed $\delta \rightarrow \delta^*$ transition.

Cotton et al.[9] reported the preparation and structure for a triclinic crystal of tetrakis(μ-pivalato)dimolybdenum(II) which

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