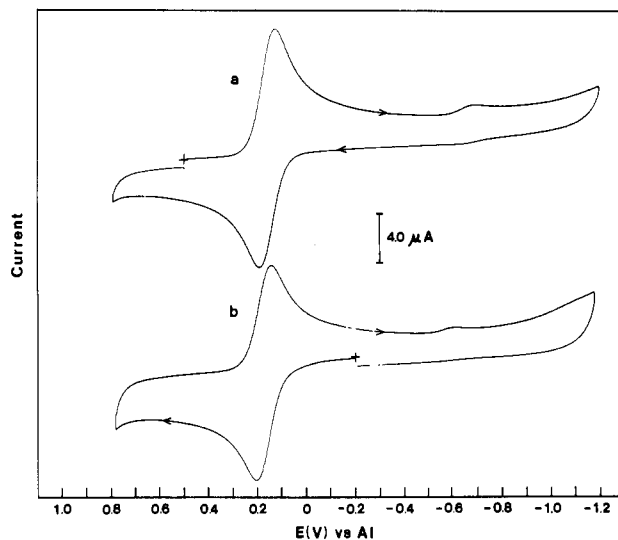# Communications

Molybdenum Chloro Complexes in Room-Temperature Chloroaluminate Ionic Liquids: Stabilization of $[MoCl_6]^{2-}$ and $[MoCl_6]^{3-}$

Sir:

We wish to report electrochemical and spectroscopic data that indicate the formation of stable solutions of the weakly solvated molybdenum(IV) and molybdenum(III) chloro complex ions, $[MoCl_6]^{2-}$ and $[MoCl_6]^{3-}$, respectively, in the room-temperature ionic liquids aluminum chloride–*N*-*n*-butylpyridinium chloride $(AlCl_3-BPC)^{1-3}$ and aluminum chloride–1-methyl-3-ethylimidazolium chloride $(AlCl_3-MEIC)$.[4] A number of transition-metal ions[5] have been shown to form stable, anionic chloro complexes in the basic[6] composition regions of these melts. No studies involving solutions containing the $[MoCl_6]^{2-}$ ion have been reported in the literature. Complexes containing this ion hydrolyze in moist air and either are insoluble or decompose in conventional aprotic molecular solvents. As a result, previous studies involving this chloro complex were limited to the solid state.[7] For conciseness, only the results obtained with the $AlCl_3$–MEIC melt will be described in detail. The results obtained for the $AlCl_3$–BPC system are, for the most part, identical.

The addition of molybdenum(V), as either $MoCl_5$ or $[Et_4N][MoCl_6]$, to basic melt results in a yellow-orange solution. Cyclic voltammetry of this solution at a glassy-carbon electrode indicates the presence of a single redox couple with a reduction peak potential of 0.138 ± 0.003 V vs. aluminum in 66.7/33.3 mol % $AlCl_3$–MEIC melt (Figure 1a). The voltammetric peak potential separation for this cyclic voltammogram was 0.062 V at a scan rate of 0.05 V/s. (The theoretical value for a one-electron reversible charge transfer is 0.062 V at 40 °C). In addition, the voltammetric peak current ratio, i_p^a/i_p^c, was 1.0 over a range of scan rates extending from 0.02 to 0.50 V/s, suggesting the absence of homogeneous reactions coupled to the charge-transfer process.[8]

(1) Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 323.
(2) Carpio, R. A.; King, L. A.; Lindstrom, R. E.; Nardi, J. C.; Hussey, C. L. *J. Electrochem. Soc.* **1979**, *126*, 1644.
(3) For reviews concerning room-temperature chloroaluminate ionic liquids see: Chum, H. L.; Osteryoung, R. A. "Ionic Liquids"; Inman, D., Lovering, D. G., Eds.; Plenum Press: New York, 1981; pp 407–423. Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*.
(4) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263.
(5) (a) Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 2723. (b) Hussey, C. L.; Laher, T. M. *Ibid.* **1981**, *20*, 4201. (c) Laher, T. M.; Hussey, C. L. *Ibid.* **1982**, *21*, 4079. (d) Nanjundiah, C.; Shimizu, K.; Osteryoung, R. A. *J. Electrochem. Soc.* **1982**, *129*, 2474. (e) Laher, T. M.; Hussey, C. L. *Inorg. Chem.*, in press.
(6) Melts containing a stoichiometric excess of organic chloride salt are considered Lewis basic; cf. ref 3.
(7) Horner, S. M.; Tyree, S. Y. *Inorg. Chem.* **1963**, *2*, 568.

Figure 1. Cyclic voltammograms of $[MoCl_6]^{x-}$ complex ions in 44.4/55.6 mol % $AlCl_3$–MEIC melt at a glassy-carbon electrode at 40.0 °C: (a) ca. $\times 10^{-3}$ M in $MoCl_5$; (b) ca. 4.8×10^{-3} M in the product obtained after electrolytic reduction of the melt solution in (a). Sweep rates were 0.050 V/s.

Table I. pCl Dependence of the $[MoCl_6]^{2-}/[MoCl_6]^{3-}$ Electrode Reaction

$E_p^{c,a}$, V	$E_{1/2}^b$, V	mol % $AlCl_3$	pCl
0.141	0.176	47.8	0.410
0.137	0.174	47.3	0.327
0.141	0.173	46.7	0.254
0.138	0.173	46.1	0.184
0.139	0.175	45.6	0.135
0.133	0.171	45.0	0.092
0.138 ± 0.003^c	0.174 ± 0.002^c		

^{a} Voltammetric reduction peak potential at a scan rate of 0.05 V/s. ^{b} GCRDE voltammetric half-wave potential at a rotation rate of 157 rad/s. ^{c} Confidence interval of 95%.

The limiting current, i_L, at a glassy-carbon rotating-disk electrode (GCRDE) for reduction of the species obtained by dissolution of molybdenum(V) in basic melt varied linearly with the square root of the electrode rotation rate. A plot of $\log ((i_L - i)/i)$ vs. *E*, constructed with GCRDE data, was linear, exhibited a slope of 0.065 V (0.062 V theoretical), and

(8) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.
(9) Lewis, J.; Nyholm, R. S.; Smith, P. W. *J. Chem. Soc. A* **1969**, 57.
(10) Hartmann, H.; Schmidt, H. J. *Z. Phys. Chem. (Wiesbaden)* **1957**, *11*, 15.

Table II. Absorption Spectroscopic Data for Molybdenum Chloro Complex Solutes

solute	solvent	λ_{max}, nm (ϵ, L/(mol cm))	ref
$[MoCl_6]^{3-}$	conc HCl	405 (46), 507 (26), 675 (1.5)	9
$[MoCl_6]^{3-}$	conc HCl	410 (50), 512 (30), 673 (1.4)	10
$[MoCl_6]^{3-}$ ^{a}	44.4/55.6 mol % AlCl₃-MEIC	439 (32), 542 (26), 685 (1.3)	this work
$[MoCl_6]^{3-}$ ^{b}	44.4/55.6 mol % AlCl₃-MEIC	439 (36), 544 (30), 685 (1.6)	this work
$[MoCl_6]^{2-}$	44.4/55.6 mol % AlCl₃-MEIC	366 (4.4 × 10³), 391 (4.5 × 10³), 451 sh^c	this work

^{a} Electrolytic reduction. ^{b} Addition of K_3MoCl_6. ^{c} Shoulder.
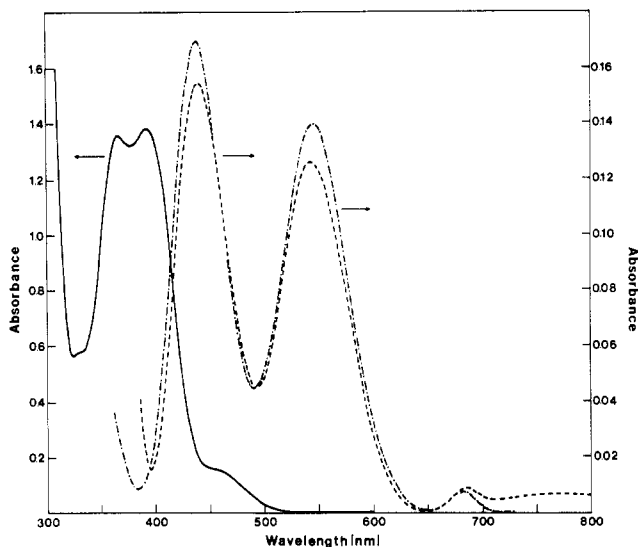
Figure 2. Absorption spectra of $[MoCl_6]^{x-}$ complex ions in 44.4/55.6 mol % AlCl₃-MEIC melt: (—) 3.1 × 10⁻⁴ M in MoCl₅; (---) ca. 4.8 × 10⁻³ M in the product obtained after electrolytic reduction of a melt solution containing MoCl₅; (—·—) 4.7 × 10⁻³ M in K₃MoCl₆.

gave a value of $E_{1/2}$ = 0.174 ± 0.003 V. Furthermore, both cyclic and GCRDE voltammetry indicate that this charge-transfer process is essentially independent of pCl in basic AlCl₃-MEIC melt (Table I).

Controlled-potential coulometry was performed on solutions of molybdenum(V) in basic melt with use of a cell constructed from a glassy-carbon crucible. Exhaustive electrolytic reduction resulted in a pink solution and gave an average n value of 1.1 ± 0.1. A cyclic voltammogram of the electrolyzed solution, initiated 200 mV negative of the solution rest potential, indicated that the reduced form of the redox couple was the only electroactive species produced during the electrolytic reduction process. Figure 2 shows absorption spectra of the basic melt both before and after reduction of the species obtained by dissolution of molybdenum(V). The spectrum obtained after electrolysis exhibits new maxima at 439, 542, and 685 nm and resembles that reported for $[MoCl_6]^{3-}$ in concentrated HCl (Table II), except that it is shifted slightly toward lower energy. In addition a spectrum very similar to that of the electrolyzed melt solution can be obtained by dissolving K₃MoCl₆ in basic melt (Figure 2 and Table II).

Taken together, the information presented above suggests that MoCl₅ and [Et₄N][MoCl₆] oxidize one or more of the components of basic melt to form the stable chloro complex ion $[MoCl_6]^{2-}$. Spectroscopic data for this species in the AlCl₃-MEIC melt are collected in Table II. The redox process depicted in Figure 1 must therefore correspond to the reversible redox couple $[MoCl_6]^{2-}/[MoCl_6]^{3-}$. The instability of molybdenum(V) in basic melt, observed in the present study, is in stark contrast to the reported stability of molybdenum solutes with this oxidation state found in basic AlCl₃-NaCl melt at 175 °C.[11]

Diffusion coefficients for the $[MoCl_6]^{2-}$ and $[MoCl_6]^{3-}$ ions in the 44.4/55.6 mol % AlCl₃-MEIC melt were calculated from GCRDE limiting-current data. At 40 °C, these values were found to be (2.7 ± 0.1) × 10⁻⁷ and (1.6 ± 0.3) × 10⁻⁷ cm²/s, respectively. Solvodynamic mean radii of 4.0 and 6.8 Å were calculated for $[MoCl_6]^{2-}$ and $[MoCl_6]^{3-}$, respectively, from these diffusion coefficients and the Stokes-Einstein equation:

$$\frac{kT}{D\pi r\eta} = 6 \qquad (1)$$

An estimate of the structural mean radius for $[MoCl_6]^{2-}$, estimated from the ionic radii of Mo^{4+} and Cl^-, is ca. 4.3 Å. The structural radius of $[MoCl_6]^{3-}$ should be slightly larger than that for $[MoCl_6]^{2-}$ as a result of the smaller charge on molybdenum(III). The close agreement between the solvo-dynamic and structural radii observed for both $[MoCl_6]^{2-}$ and $[MoCl_6]^{3-}$ suggests that the solvation of these ions is negligible in basic melt.

The small reduction waves that appear in Figure 1 at ca. -0.60 to -0.65 V increased in size substantially after the addition of oxide ion to the melt brought about by dissolution of Li₂CO₃. This behavior is similar to that observed for titanium(IV) in basic AlCl₃-BPC, and it suggests that these reduction waves are due to small amounts of a molybdenum-(IV) oxychloro complex, resulting from interaction of the molybdenum(IV) chloro complex solute with adventitious oxide ion (as $AlOCl_2^-$).[12] It is interesting to note that a molybdenum(IV) oxychloride compound, MoOCl₂, has been reported,[13] but there is a paucity of data concerning molybdenum(IV) oxychloro complexes in the literature. Further studies of molybdenum solutes in room-temperature chloroaluminate melts, particularly oxychloro complexes, are in progress in our laboratories.

Registry No. $[MoCl_6]^{2-}$, 44440-42-8; $[MoCl_6]^{3-}$, 15203-34-6; MoCl₅, 10241-05-1; [Et₄N][MoCl₆], 4113-73-9; Mo, 7439-98-7; AlCl₃, 7446-70-0; MEIC, 65039-09-0; BPC, 1124-64-7.

(11) Phillips, J.; Osteryoung, R. A. *J. Electrochem. Soc.* **1977**, *124*, 1465.

(12) Linga, H.; Stojek, Z.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 3754.

(13) Schafer, H.; Tillack, J. *J. Less-Common Met.* **1964**, *6*, 152.

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