

ligands are not merely spectator ligands, but participate actively in the photophysical processes.

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Electrochemistry and Spectroelectrochemistry of Polynuclear Rhenium(III) Chloride Cluster Complexes and Their One-Electron-Reduction Products in a Basic Room-Temperature Chloroaluminate Molten Salt

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The dimeric, metal-metal-bonded rhenium(III) complex $[\text{Re}_2\text{Cl}_8]^{2-}$ is stable in the basic aluminum chloride-1-methyl-3-ethylimidazolium chloride ($\text{AlCl}_3\text{-MeEtimCl}$) molten salt and can be reduced to $[\text{Re}_2\text{Cl}_8]^{3-}$ at a glassy-carbon electrode in a reversible electrode reaction with a voltammetric half-wave potential, $E_{1/2}$, of ca. -0.58 V in the 49.0/51.0 mol % melt versus the Al^{3+}/Al couple in the 66.7/33.3 mol % melt at $40\text{ }^\circ\text{C}$. It is possible to electrochemically generate stable, bulk solutions containing $[\text{Re}_2\text{Cl}_8]^{3-}$, provided that oxygen is rigorously excluded from the electrochemical cell. The average Stokes-Einstein products for $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_2\text{Cl}_8]^{3-}$ are 2.0×10^{-10} and $1.2 \times 10^{-10}\text{ g cm s}^{-2}\text{ K}^{-1}$, respectively. The addition of Re_2Cl_8 to basic $\text{AlCl}_3\text{-MeEtimCl}$ produces the trimeric, metal-metal-bonded rhenium(III) complex $[\text{Re}_3\text{Cl}_{12}]^{3-}$. This species can also be reduced at a glassy-carbon electrode in a one-electron, reversible electrode reaction with an $E_{1/2}$ of about -0.34 V in this same basic melt. However, $E_{1/2}$ for this reaction is dependent upon the pCl of the melt, indicating the loss of chloride ion from the coordination sphere of the cluster during reduction to form a species of the type $[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$ for which x may be 1. It is possible to electrochemically generate stable solutions of this reduced species in the absence of oxygen. The average Stokes-Einstein products for $[\text{Re}_3\text{Cl}_{12}]^{3-}$ and its one-electron-reduction product are 1.3×10^{-10} and $1.0 \times 10^{-10}\text{ g cm s}^{-2}\text{ K}^{-1}$, respectively. Both $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_3\text{Cl}_{12}]^{3-}$ exhibit an additional multielectron voltammetric reduction process at potentials negative of their one-electron reduction waves. In both cases, bulk electrolysis experiments conducted at potentials negative of these very large waves destroyed the parent clusters. In basic melt at temperatures of ca. $175\text{ }^\circ\text{C}$ or more, each $[\text{Re}_3\text{Cl}_{12}]^{3-}$ ion is irreversibly converted to one $[\text{Re}_2\text{Cl}_8]^{2-}$ ion. Absorption spectroscopic data for $[\text{Re}_2\text{Cl}_8]^{2-}$, $[\text{Re}_3\text{Cl}_{12}]^{3-}$, and their one-electron-reduction products are reported.

Introduction

The combination of aluminum chloride and certain quaternary ammonium chloride salts, notably 1-(1-butyl)pyridinium chloride (BupyCl) or 1-methyl-3-ethylimidazolium chloride (MeEtimCl), produces molten salts or ionic liquids that are molten at room temperature.¹ The Lewis acid-base properties of these chloroaluminate molten salts can be controlled by adjusting the ratio of aluminum chloride to organic salt. Those melts containing a molar excess of aluminum chloride are designated as "acidic" because they have been shown to contain the chloride ion acceptor Al_2Cl_7^- while those containing a molar excess of the organic chloride salt are considered to be basic because they contain chloride ion that is not covalently bound to aluminum. Basic room-temperature chloroaluminate ionic liquids have been shown to be expedient solvents for studying the electrochemistry and absorption spectroscopy of a wide variety of highly charged anionic transition-metal chloride complexes;² in many cases they have proven to be superior to conventional molecular solvents like water, acetonitrile, and dichloromethane and to high-temperature molten salts like the alkali-metal chlorides and the alkali-metal chloride based chloroaluminates. The important factors that contribute to the utility of these molten salts as solvents for characterizing these complexes have been discussed at length.^{2,3} One disadvantage of room-temperature chloroaluminate molten salts is that they and their components are extremely moisture sensitive and must be handled only in a glovebox with a very dry atmosphere or in sealed vessels.

Metal-metal-bonded, polynuclear transition-metal clusters, which are differentiated from classical polynuclear species or Werner complexes in which the component metal atoms may share ligands but do not otherwise interact, are of great interest as a result of their bonding, structures, and reactivities. The chemistry of rhenium(III) is especially fertile with regard to polynuclear metal clusters, and two anionic chloride cluster complexes, $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_3\text{Cl}_{12}]^{3-}$, are well-known. The former complex possesses a quadruple metal-metal bond with a Re-Re distance of about 0.22 nm^4 while the latter, which exists as a triangular arrangement of metal atoms with two sets of double bonds per atom, exhibits a slightly longer Re-Re separation of about 0.25 nm^5 .

Reports describing the electrochemistry of $[\text{Re}_2\text{Cl}_8]^{2-}$ are conflicting. For example, Cotton and co-workers⁶ reported two one-electron polarographic reduction waves for $[\text{Re}_2\text{Cl}_8]^{2-}$ in acetonitrile at a dropping-mercury electrode (DME). A later cyclic voltammetric study of this complex by Hendriksma and van Leeuwen⁷ at a hanging-mercury-drop electrode (HMDE) also revealed two one-electron reduction processes. The first reduction reaction was reported to be electrochemically reversible, but the product of this reaction was only moderately stable on the voltammetric time scale while the two-electron-reduction product was found to be completely unstable. A subsequent voltammetric examination of $[\text{Re}_2\text{Cl}_8]^{2-}$ at a platinum electrode in both acetonitrile and dichloromethane revealed only a *single* one-electron, quasireversible electrode reaction.⁸ The one-electron-reduction

(1) For reviews see: (a) Chum, H. L.; Osteryoung, R. A. In *Ionic Liquids*; Inman, D., Lovering, D. G., Eds.; Plenum: New York, 1981; pp 407-423. (b) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185-230. (c) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. 1, pp 55-78. (2) Hussey, C. L. *Pure Appl. Chem.* **1988**, *60*, 1763. (3) Appleby, D.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Nature* **1986**, *323*, 614.

(4) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982; pp 40-41.

(5) See ref 4, pp 266-267.

(6) Cotton, F. A.; Robinson, W. R.; Walton, R. A. *Inorg. Chem.* **1967**, *6*, 1257.

(7) Hendriksma, R. R.; van Leeuwen, H. P. *Electrochim. Acta* **1973**, *18*, 39.

(8) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 383.

Table I. Summary of Spectroscopic Data for Rhenium Chloride Cluster Complexes

solute	solvent	λ , nm (ϵ , M ⁻¹ cm ⁻¹)	ref
[Bu ₄ N] ₂ [Re ₂ Cl ₈]	49.0/51.0 mol %	253 (1.0 × 10 ⁴), 316 (1.0 × 10 ⁴), ~360, ^{a,b} 688 (2.3 × 10 ³)	this work
[Bu ₄ N] ₂ [Re ₂ Cl ₈]	44.4/55.6 mol % AlCl ₃ -MeEtimCl	252 (1.1 × 10 ⁴), 311 (1.1 × 10 ⁴), ~360, ^{a,b} 684 (2.4 × 10 ³)	this work
[Bu ₄ N] ₂ [Re ₂ Cl ₈]	CH ₃ CN	250 (1.0 × 10 ⁴), 307 (8.7 × 10 ³), 680 (2.3 × 10 ³)	17
[Re ₂ Cl ₈] ³⁻ ^c	49.0/51.0 mol % AlCl ₃ -MeEtimCl	268 (7.5 × 10 ³), ~305 (1.9 × 10 ³), ^d 512 (2.3 × 10 ²), 580 (2.8 × 10 ²), 708, ^b ~830 ^b	this work
Re ₃ Cl ₉	49.0/51.0 mol % AlCl ₃ -MeEtimCl	297 (1.3 × 10 ⁴), 319 (1.5 × 10 ⁴), 347 (1.0 × 10 ⁴), 420 (1.0 × 10 ³), 530 (1.7 × 10 ³), 790 (4.2 × 10 ²)	this work
Re ₃ Cl ₉	44.4/55.6 mol % AlCl ₃ -MeEtimCl	295 (1.4 × 10 ⁴), 319 (1.5 × 10 ⁴), 349 (1.1 × 10 ⁴), 419 (1.2 × 10 ³), 530 (1.9 × 10 ³), 788 (5.5 × 10 ²)	this work
Re ₃ Cl ₉	12 M aqueous HCl	285 (9.8 × 10 ³), 313 (1.2 × 10 ⁴), 340 (8.9 × 10 ³), 400, ^d 522 (1.9 × 10 ³), 774 (4.7 × 10 ²)	this work
Cs ₃ [Re ₃ Cl ₁₂]	aqueous HCl	315 (9.2 × 10 ³), 339 (7.2 × 10 ³), 400 (1.3 × 10 ³), 520 (1.7 × 10 ³), 770 (4.6 × 10 ²)	11
[Re ₃ Cl _{12-x}] ^{(4-x)-} ^c	44.4/55.6 mol % AlCl ₃ -MeEtimCl	285 (1.2 × 10 ⁴), 540 (1.0 × 10 ³), 890 (5.2 × 10 ²)	this work

^a Broad band composed of two or more maxima. ^b Very weak. ^c Produced by electrolytic reduction of the parent complex. ^d Shoulder.

product, believed to be [Re₂Cl₈]³⁻, was unstable in both solvents on the voltammetric time scale.

Very little information is available about the electrochemistry of [Re₃Cl₁₂]³⁻ in any kind of solvent. Münze⁹ observed a single, pCl-dependent, six-electron reduction wave for this species at a DME in 0.5 M aqueous HCl and proposed that one chloride ion is lost from the axial position on each rhenium atom during the reduction process. Schub and Gross¹⁰ used electrochemistry and absorption spectroscopy to investigate the hydrolysis of [Re₃Cl₁₂]³⁻ in aqueous HCl and KCl solutions; two reduction waves, the height of the first wave being approximately 33% of the height of the second, were found for this complex at a DME. A limited investigation of trinuclear rhenium(III) chloride species was also undertaken in molten media.¹¹ Re₃Cl₉ was found to be stable in molten dimethyl sulfone at temperatures of up to 200 °C, but [Re₃Cl₁₂]³⁻ was rapidly converted to [Re₂Cl₈]²⁻ when added to this solvent at this temperature. Re₃Cl₉ was observed to disproportionate to rhenium metal and [ReCl₆]²⁻ in the LiCl-KCl eutectic.¹¹

In this article, we report the electrochemical and spectroelectrochemical characterization of [Re₂Cl₈]²⁻ and [Re₃Cl₁₂]³⁻ and their one-electron-reduction products in the basic AlCl₃-MeEtimCl molten salt. In addition, we describe some of the conditions that lead to the conversion of [Re₃Cl₁₂]³⁻ to [Re₂Cl₈]²⁻ in this ionic solvent.

Experimental Section

Apparatus. Electrochemical and spectroelectrochemical experiments were conducted under a highly purified nitrogen atmosphere inside a Kewaunee Scientific Equipment Corp. (KSE) glovebox. The glovebox was equipped with a KSE Model 2C2500 30 ft³ min⁻¹ inert-gas purifier. The procedure used to monitor the oxygen and moisture content of this glovebox has been described.¹² Cyclic and rotating-disk-electrode (RDE) voltammetry and chronoamperometry experiments were performed with an AMEL Model 551 potentiostat, an AMEL Model 566 function generator, an EG & G Princeton Applied Research Corp. Model 379 digital coulometer, and a Pine Instruments Co. Model AFMSR electrode rotator. Spectroelectrochemical experiments were carried out in the glovebox in a 1 mm path length microcell containing a reticulated glassy-carbon optically transparent electrode (RGC-OTE) by using a microprocessor-controlled, fiber optic based spectrophotometry system¹³ and an AMEL Model 552 high-voltage potentiostat. The useful wavelength range of this spectrophotometry system extended from ca. 380 to 900 nm. Electrochemical data were recorded by using either a Houston Instruments Model 100 X-Y/Y-T recorder, a Nicolet Explorer I digital oscilloscope, or a Hewlett-Packard Model 3467A logging multimeter. Electronic resistance compensation was employed during all electrochemical experiments except bulk controlled-potential electrolysis.

The glassy-carbon/Pyrex glass (GC) working electrode (area = 0.066 cm²) that was used for conventional voltammetric and chronoampero-

metric experiments, including RDE voltammetry (RDE), the electrochemical cell, and the furnace that was used to heat this cell were identical with those described in a previous article.¹⁴ Bulk electrolysis experiments were carried out in this same cell except that the GC electrode was replaced by a large surface area platinum-gauze electrode. Aluminum wires (Alfa, m5N) served as the counter and reference electrodes. All potentials are reported versus the Al³⁺/Al couple in the nominal 66.7/33.3 mol % melt. The potential of this reference electrode was reproducible to within approximately ±10 mV. Unless specified otherwise, all electrochemical and spectroelectrochemical experiments were performed at 40 °C.

Conventional absorption spectra were recorded by using either a Perkin-Elmer Model 3840 Lambda Array or a Perkin-Elmer Hitachi Model 200 UV-vis spectrophotometer. Near-infrared spectra were recorded by using a Cary 17 spectrophotometer. Spectra were recorded in either 10 or 1 mm path length fused silica cells that were fitted with airtight Teflon caps. In order to record spectra over the temperature range extending from 40 to 200 °C, the former instrument was equipped with a small furnace of our own design. This furnace was constructed from an aluminum block and a 150-W Vulcan Electric cartridge heater, and it had a water-cooled base. The temperature of this furnace could be controlled to ±5 °C by using a variable voltage transformer (Variac).

Chemicals. Rhenium(III) chloride (Johnson Matthey, 99.9%) was used as received. Tetrabutylammonium octachlorodirhenate(III), [Bu₄N]₂[Re₂Cl₈], was prepared according to the procedure described by Barder and Walton¹⁵ with the exception that the reaction was performed in a 190 mm × 40 mm Pyrex glass vessel sealed with a vacuum-tight Teflon stopcock. Aluminum chloride (Fluka, puriss) was sublimed in vacuo from an AlCl₃-NaCl melt a minimum of three times before use. The procedures used to synthesize and purify the MeEtimCl salt were the same as those described previously.¹⁶ Ethylaluminum dichloride (Aldrich) was used as received.

Results and Discussion

[Bu₄N]₂[Re₂Cl₈]. An absorption spectrum of a solution prepared by dissolving [Bu₄N]₂[Re₂Cl₈] in the 49.0/51.0 mol % AlCl₃-MeEtimCl melt is shown in Figure 1a. The wavelengths and molar absorptivities of the more prominent bands that appear in this spectrum and a similar spectrum that was recorded for a solution prepared from the 44.4/55.6 mol % melt are collected in Table I along with literature data for this compound dissolved in CH₃CN. The spectroscopic data originating from the melt solutions are in good agreement with the literature data, indicating that [Re₂Cl₈]²⁻ is indeed present in the basic AlCl₃-MeEtimCl molten salt. It is also possible to detect some additional very weak bands at about 572, 475, and 422 nm and in the 372–360-nm region when the spectrum in Figure 1a is expanded (Figure 1b). The electronic transitions associated with these bands are discussed by Trogler et al.¹⁸ The addition of [Bu₄N]₂[Re₂Cl₈] to neutral

(14) Scheffler, T. B.; Hussey, C. L. *Inorg. Chem.* **1984**, *23*, 1926.

(15) Barder, T. J.; Walton, R. A. *Inorg. Synth.* **1985**, *23*, 116.

(16) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263.

(17) Cotton, F. A.; Curtis, N. F.; Johnson, B. F. G.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 326.

(18) Trogler, W. C.; Cowman, C. D.; Gray, H. B.; Cotton, F. A. *J. Am. Chem. Soc.* **1977**, *99*, 2993.

(9) (a) Münze, R. Z. *Phys. Chem. (Leipzig)* **1964**, *226*, 415. (b) Münze, R. Z. *Phys. Chem. (Leipzig)* **1969**, *240*, 135.

(10) Schub, J. M.; Gross, M. *Electrochim. Acta* **1975**, *20*, 227.

(11) Bailey, R. A.; McIntyre, J. A. *Inorg. Chem.* **1966**, *5*, 1940.

(12) Sun, J.-W.; Hussey, C. L. *Inorg. Chem.* **1989**, *28*, 2731.

(13) Ward, E. H.; Hussey, C. L. *Anal. Chem.* **1987**, *59*, 213.

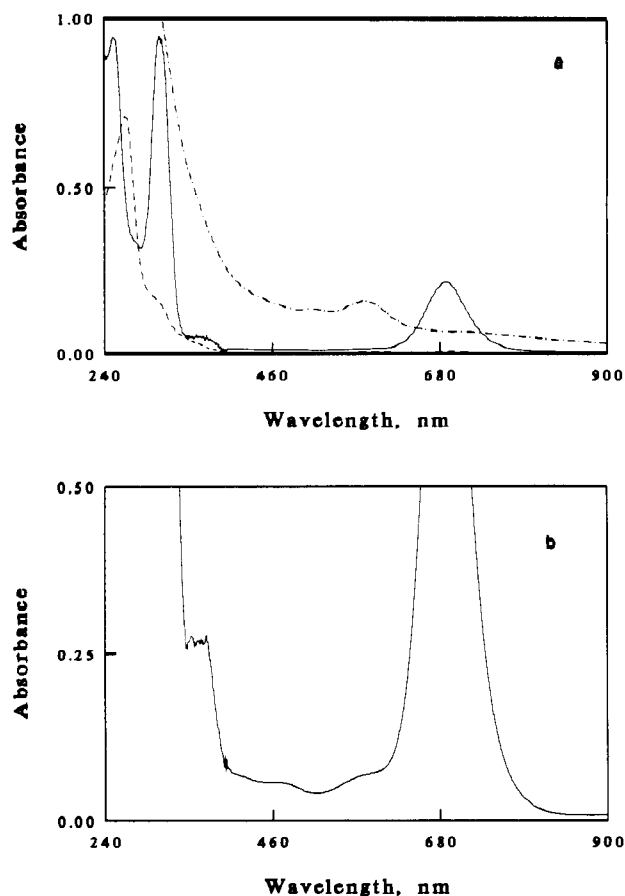


Figure 1. Absorption spectra of dimeric rhenium chloride complexes in the 49.0/51.0 mol % AlCl_3 -MeEtimCl molten salt at room temperature: (a) (—) 9.07×10^{-4} M $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$, (---) 9.53×10^{-4} M solution of $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ after exhaustive reduction at -0.71 V, and (-·-) 5.73×10^{-3} M solution of $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ after exhaustive reduction at the same potential; (b) 4.52×10^{-3} M $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$. The cell path lengths were 1.00 mm.

and acidic AlCl_3 -MeEtimCl resulted in a purple precipitate that is identical in appearance with Re_3Cl_9 . If this precipitate is indeed Re_3Cl_9 , then the precipitation process results in the transformations of the Re_2^{6+} core to the Re_3^{9+} core. However, such conversions are not without precedent; Walton and co-workers¹⁹ observed the conversion of the rhenium(III) acetates $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{X}_2$, where $\text{X} = \text{Cl}$ or Br , to Re_3X_9 upon their reaction with HCl or HBr .

A cyclic voltammogram of $[\text{Re}_2\text{Cl}_8]^{2-}$ in the 49.0/51.0 mol % melt, covering the nominal electroactive window of the ionic solvent, is shown in Figure 2a. The principal features of this voltammogram are a small reduction wave with a peak potential, E_p , of about -0.61 V and a much larger reduction process with two closely spaced peaks, the first peak in this wave appearing at around -1.44 V. Only the first reduction wave at $E_p = -0.61$ V (enlarged in Figure 2a for clarity) exhibits a reverse current. The average cyclic voltammetric peak potential separation, ΔE_p , for this wave was 0.062 V over the range of scan rates from 0.010 to 0.200 V s^{-1} ; this value is in excellent agreement with the theoretical value of 0.062 V expected for a one-electron, reversible electrode reaction at 40°C . In addition, the peak current ratio, i_p^a/i_p^c , for this wave, which was calculated by using Nicholson's empirical procedure,²⁰ was 1.0, and the peak current function, $i_p^c/v^{1/2}$, where v is the scan rate, was essentially constant over this same range of scan rates. The GCRDE limiting current, i_L , divided by the square root of the angular velocity of the electrode was constant over the range of angular velocities extending from 105 to 209 rad s^{-1} . Virtually identical results were observed for

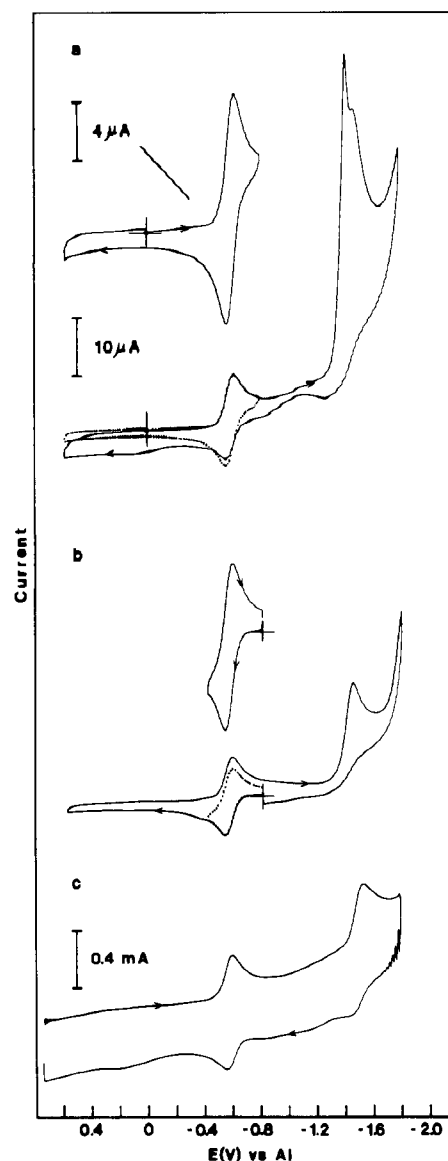


Figure 2. Cyclic voltammograms of dimeric rhenium chloride complexes at a glassy-carbon electrode in the 49.0/51.0 mol % AlCl_3 -MeEtimCl molten salt at 40.0°C : (a) 3.55×10^{-3} M $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ at a scan rate of 50 mV s^{-1} ; (b) solution in (a) after exhaustive reduction at -0.71 V (note: the current scales and scan rate are the same as those in (a)); (c) 5.73×10^{-3} M $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ at a scan rate of 20 V s^{-1} .

these same parameters in the 44.4/55.6 mol % melt.

Electrochemical data for the first reduction process are collected in Table II. The values that appear in this table are the average values from several experiments at different concentrations. A shift in the voltammetric half-wave potential, $E_{1/2}$, for the reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$ with melt composition is apparent upon close inspection of the data appearing in this table. Since the calculated chloride ion activities in the 49.0/51.0 and 44.4/55.6 mol % melts differ by 1 order of magnitude, this shift in potential is actually quite small, amounting to only 0.020 V/pCl unit. Shifts in $E_{1/2}$ with melt composition²¹ of similar magnitude have been noted for a number of other transition-metal redox systems that exhibit the same chloride coordination after reduction, e.g., $[\text{IrCl}_6]^{2-/3-}$ (0.022 V/pCl unit)²² and $[\text{WCl}_6]^{-2/2-}$ (0.018 V/pCl unit).¹⁴ We

(19) (a) Glicksman, H. D.; Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205. (b) Glicksman, H. D.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 200.
(20) Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406.

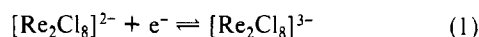
(21) For an electrochemical reaction of the type $[\text{MCl}_x]^{n-x} + ze^- \rightleftharpoons [\text{MCl}_x]^{n-z} + (x-y)\text{Cl}^-$, a negative shift in $E_{1/2}$ of approximately $2.3(x-y)RT/zF$ volts per unit decrease in pCl is expected, e.g., a negative shift of approximately 0.062 V for $z = x - y = 1$ at 40°C . In practice, we find that this method is not especially reliable for estimating $x - y$ since negative shifts in $E_{1/2}$ with decreasing pCl on the order of 15 – 25 mV/pCl unit are almost always observed for redox systems in room-temperature chloroaluminate melts, even when $x - y = 0$. One possible explanation for these shifts has been advanced; cf. ref 22.

Table II. Summary of Electrochemical Data for Rhenium(III) Chloride Cluster Complexes and Their One-Electron-Reduction Products in Basic $\text{AlCl}_3\text{-MeEtImCl}$ at 40 °C

complex	mol % AlCl_3	E_p^a , V	$E_{1/2}^b$, V	$E_{1/2}^c$, V	$10^7 D_r^d$, $\text{cm}^2 \text{s}^{-1}$	$10^{10} \eta D_r / T$, $\text{g cm s}^{-2} \text{K}^{-1}$	$E^{\circ'}$, V
$[\text{Re}_2\text{Cl}_8]^{2-}$	49.0	-0.609	-0.577	-0.576	4.61	1.9 ± 0.2	
$[\text{Re}_2\text{Cl}_8]^{3-}$ ^f	49.0	-0.538	-0.572	-0.578	2.56	1.1 ± 0.2	-0.566
$[\text{Re}_3\text{Cl}_{12}]^{3-}$	49.0	-0.371	-0.341	-0.344	3.09	1.3 ± 0.2	
$[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$ ^f	49.0	-0.306	-0.342	-0.338	2.27	1.0 ± 0.2	-0.337
$[\text{Re}_2\text{Cl}_8]^{2-}$	44.4	-0.629	-0.594	-0.599	2.99	2.0 ± 0.1	
$[\text{Re}_2\text{Cl}_8]^{3-}$ ^f	44.4	-0.556	-0.588	-0.589	1.93	1.3 ± 0.1	-0.589
$[\text{Re}_3\text{Cl}_{12}]^{3-}$	44.4	-0.471	-0.439	-0.436	1.83	1.2 ± 0.1	
$[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$ ^f	44.4	-0.398	-0.432	-0.437	1.43	0.9 ± 0.1	-0.434

^a Average voltammetric peak potential over the range of scan rates from 0.01 to 0.20 V s^{-1} . All potentials are referenced to the Al^{3+}/Al couple in the 66.7/33.3 mol % melt. The oxidation of ferrocene was observed at approximately 0.24 V versus this reference electrode. ^b Estimated from cyclic voltammetric peak potentials by using $(E_p^c + E_p^a)/2$. ^c Average GCRDE value over the range of angular velocities from 105 to 209 rad s^{-1} . ^d Average value from stationary- and rotating-electrode voltammetry and chronoamperometry. ^e Formal potential estimated from $E_{1/2}$, D_R , and D_O by using $E^{\circ'} = E_{1/2} + 0.027 \ln (D_O/D_R)^{2/3}$. ^f Produced by electrolytic reduction of the parent complex.

infer from the size of the shift seen for $[\text{Re}_2\text{Cl}_8]^{2-}$ that this species also retains the same coordination after reduction. Taken together, the foregoing electrochemical and spectroscopic results suggest that the first reduction wave corresponds to the reversible, one-electron reaction



in which $[\text{Re}_2\text{Cl}_8]^{3-}$ is stable on the voltammetric time scale. These results differ greatly from those observed in acetonitrile where this electrode reaction was found to be quasireversible and $[\text{Re}_2\text{Cl}_8]^{3-}$ was found to exhibit limited stability.⁸

In view of the fact that considerable unsuccessful effort has been directed by several research groups^{7,8} in the recent past toward the production of stable solutions of $[\text{Re}_2\text{Cl}_8]^{3-}$ in molecular solvents, we next investigated the bulk, controlled-potential electrolytic reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$ in an attempt to produce a stable solution of $[\text{Re}_2\text{Cl}_8]^{3-}$. These experiments were conducted at an applied potential of -0.71 V at a platinum-gauze working electrode. The initial segment of a plot of $\log i$ versus t , which was constructed from the electrolysis current-time data recorded during one of these experiments, was linear and gave an n value of approximately 1. However, at longer times $\log i$ was not linearly dependent on t and, in fact, became almost independent of t . Overall, the shape of this plot was quite similar to that typically observed for an electrode reaction complicated by a very slow, coupled homogeneous chemical reaction in which the original electroactive species was regenerated, i.e., a so-called "catalytic process".²³ This catalytic process was found to arise from a reaction between the reduced species and trace amounts of oxygen in the glovebox atmosphere. This result was unexpected because a 25-W light bulb with its filament exposed to this same glovebox atmosphere would remain lighted for almost 1 week. However, if similar controlled-potential electrolysis experiments were conducted shortly after regeneration of the glovebox purification system, it was possible to reduce virtually all of the $[\text{Re}_2\text{Cl}_8]^{2-}$, as judged by scans with the GCRDE. Cyclic voltammograms of the solution in Figure 2a, resulting from exhaustive reduction at -0.71 V, are shown in Figure 2b, and data taken from this and several additional experiments in both the 49.0/51.0 and 44.4/55.6 mol % melts are collected in Table II. It is obvious that $[\text{Re}_2\text{Cl}_8]^{3-}$ is now the principal electroactive species in the solution since the value of $E_{1/2}$ for the oxidation of this species (Table II) is almost identical with the $E_{1/2}$ value for the reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$. To the best of our knowledge, this is the first time that a stable solution of this species has been prepared.

The color change associated with the reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$ to $[\text{Re}_2\text{Cl}_8]^{3-}$ was subtle. Solutions containing the former were blue-green and changed to navy blue after reduction at -0.71 V.

The reduced solutions were stable for several days, provided that strict precautions were taken to exclude all traces of oxygen from the storage vessel. If these solutions were exposed to oxygen in the atmosphere, $[\text{Re}_2\text{Cl}_8]^{3-}$ reverted back to $[\text{Re}_2\text{Cl}_8]^{2-}$ in a matter of minutes. As a consequence of this reactivity toward oxygen, it was very difficult to obtain a high-quality spectrum of a reduced solution outside the glovebox, even in a cuvette with a supposedly airtight cap. Nevertheless, an absorption spectrum of a completely reduced solution of $[\text{Re}_2\text{Cl}_8]^{2-}$ ostensibly containing only $[\text{Re}_2\text{Cl}_8]^{3-}$ is shown in Figure 1a. Data taken from this spectrum are recorded in Table I. Note that the intense band at 688 nm that is characteristic of $[\text{Re}_2\text{Cl}_8]^{2-}$ is absent from the spectrum of the reduced species and that new bands are present at 268, 305, 512, 580, 708, and ca. 830 nm. The $[\text{Re}_2\text{Cl}_8]^{3-}$ anion is predicted to exhibit an absorption maximum in the near-infrared region at ca. 1400 nm.^{24a} A near-infrared absorption spectrum of a reduced solution of $[\text{Re}_2\text{Cl}_8]^{2-}$ did in fact exhibit a fairly intense band with considerable vibrational fine structure centered at 1460 nm, in excellent agreement with this prediction and with the observation of a band at 1503 nm for $[\text{Re}_2\text{Cl}_4(\text{PR}_3)_4]^+$ ($R = \text{alkyl}$),^{24b} which possesses an analogous Re_2^{5+} core. The $[\text{Re}_2\text{Cl}_8]^{3-}$ spectrum will be discussed in greater detail in a future communication from this laboratory.

Spectroelectrochemical experiments were conducted in the glovebox in order to substantiate the one-electron nature of the $[\text{Re}_2\text{Cl}_8]^{2-}$ bulk reduction reaction and in order to directly observe the spectral changes attendant to the reduction of this species in a nominally oxygen-free environment. These experiments were carried out by applying selected potential steps to an RGC-OTE cell (vide supra) that contained a dilute solution of $[\text{Re}_2\text{Cl}_8]^{2-}$. Absorption spectra were recorded after equilibrium was established, i.e., after the cell current had decayed to the background level following the application of each potential step. The applied potential, E , controls the concentration ratio, $[\text{Red}]/[\text{Ox}]$, through the Nernst equation. This ratio is in turn reflected in the absorption spectrum recorded at each potential. The relationship between E , the formal electrode potential of the redox couple, $E^{\circ'}$, and the measured absorbance of the RGC-OTE cell is

$$E = E^{\circ'} + 2.3(RT/nF) \log [(A_R - A)/(A - A_O)] \quad (2)$$

where A_O , A , and A_R are the absorbances of the cell containing only the fully oxidized species, a mixture of the oxidized and reduced species, and only the reduced species, respectively, at a selected wavelength. The results of one of these spectropotentiostatic experiments are shown in Figure 3. The slope of a plot based on eq 2 in which the absorbance was monitored at 688 nm is 0.066 V (Figure 3, inset). This value is in very good agreement with the theoretical 0.062-V Nernst slope expected for a one-electron redox couple at 40.0 °C. The $[\text{Re}_2\text{Cl}_8]^{3-}$ that was pro-

(22) Sun, J.-W.; Ward, E. H.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Inorg. Chem.* **1987**, *26*, 2140.
(23) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 476-478.

(24) (a) Ebner, J. R.; Walton, R. A. *Inorg. Chim. Acta* **1975**, *14*, L45. (b) Bursten, B. E.; Cotton, F. A.; Fanwick, P. E.; Stanley, G. G.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 2606.

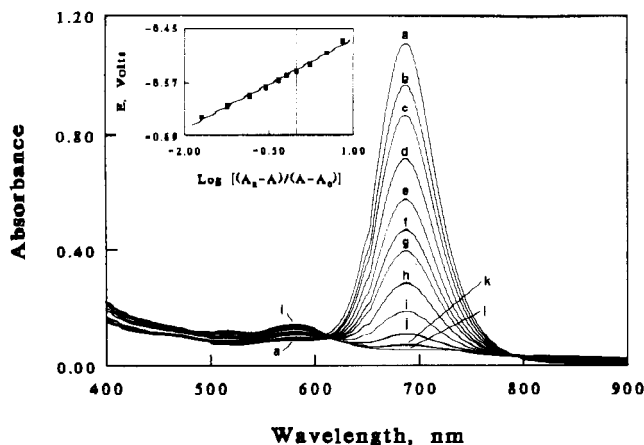


Figure 3. Absorption spectra of a 5.53×10^{-3} M solution of $[\text{Bu}_4\text{N}]_2\text{[Re}_2\text{Cl}_8]$ in the 49.0/51.0 mol % $\text{AlCl}_3\text{-MeEtimCl}$ molten salt at 40.0 °C in the RGC-OTE cell at various applied potentials (V): (a) open circuit; (b) -0.480 ; (c) -0.506 ; (d) -0.529 ; (e) -0.545 ; (f) -0.556 ; (g) -0.565 ; (h) -0.581 ; (i) -0.600 ; (j) -0.625 ; (k) -0.648 ; (l) -0.800 . Inset: Nernst plot constructed from these spectra.

duced during this experiment could be converted back to $[\text{Re}_2\text{Cl}_8]^{2-}$ quantitatively by applying the appropriate potential to the RGC-OTE electrode.

As pointed out above, solutions of $[\text{Re}_2\text{Cl}_8]^{2-}$ exhibit an additional voltammetric reduction process at potentials negative of the one-electron reduction wave (Figure 1a). The current associated with this reduction process is substantially greater than that for the simple one-electron reduction wave at $E_p = -0.61$ V, suggesting that this large wave arises from a multielectron reduction reaction. At present, we can not provide an explanation for the origin of this exalted wave; however, we do offer the following observations about it. The reduction wave at $E_p = -1.48$ V appears to be preceded by a symmetrical prewave at $E_p = -1.44$ V, which is similar to that observed in the case of strong adsorption of the reduction product,²⁵ but the current for this prewave was not particularly reproducible. It was necessary to clean the electrode surface each time these waves were traversed in order to remove an insoluble film that blocked the electrode surface. Also, it was possible to observe curve crossing²⁶ in the -0.9 to -1.3 V potential region on the reverse scan, but only on the first scan after the electrode was freshly polished and if the scan was reversed immediately after the peak at -1.48 V was traversed. When the scan is reversed at -1.8 V prior to the melt limit, there are no really well-defined oxidation waves associated with either of the reduction processes other than that ascribed to the oxidation of $[\text{Re}_2\text{Cl}_8]^{3-}$. However, some essentially featureless oxidation current can be observed after the $[\text{Re}_2\text{Cl}_8]^{3-}$ oxidation wave is traversed on the positive scan (Figure 2a). At very fast scan rates, the prewave disappears and the wave at $E_p = -1.48$ V approaches the height of the $[\text{Re}_2\text{Cl}_8]^{2-}$ reduction wave (Figure 2c). Also, the current for the reduction wave at -1.48 V diminishes and the prewave disappears when the voltammetric scans are conducted in solutions containing only $[\text{Re}_2\text{Cl}_8]^{3-}$ (Figure 2b). These results suggest that $[\text{Re}_2\text{Cl}_8]^{2-}$ may be involved in the coupled homogeneous chemistry that contributes to the large current for this reduction process. Removal of all adventitious protonic impurities from the melt with ethylaluminum dichloride²⁷ had no effect whatsoever on either the size or shape of the waves seen in Figure 2a. Bulk controlled-potential electrolysis experiments that were conducted at -1.60 V destroyed the dimeric cluster and produced a brown suspension in the melt that we were unable to identify.

(25) Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514.

(26) Cyclic voltammetric curve crossing is often associated with nucleation rate controlled metal deposition reactions and with the electrochemical induction of chemical reactions (cf.: Amatore, C.; Pinson, J.; Saveant, J. M.; Thiebault, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *107*, 59).

(27) Zawodzinski, T. A.; Carlin, R. T.; Osteryoung, R. A. *Anal. Chem.* **1987**, *59*, 2639.

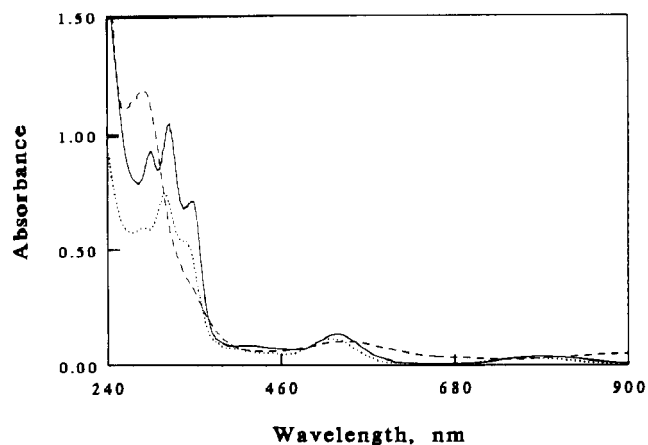


Figure 4. Absorption spectra of trimeric rhenium chloride complexes at room temperature: (—) 6.82×10^{-4} M Re_3Cl_9 in the 44.4/55.6 mol % $\text{AlCl}_3\text{-MeEtimCl}$ molten salt (cell path length was 1.00 mm), (---) 1.02×10^{-3} M solution of Re_3Cl_9 in the 44.4/55.6 mol % melt after exhaustive reduction at -0.55 V (cell path length was 1.00 mm), and (···) 6.05×10^{-3} M Re_3Cl_9 in 12 M HCl (cell path length was 1.00 cm).

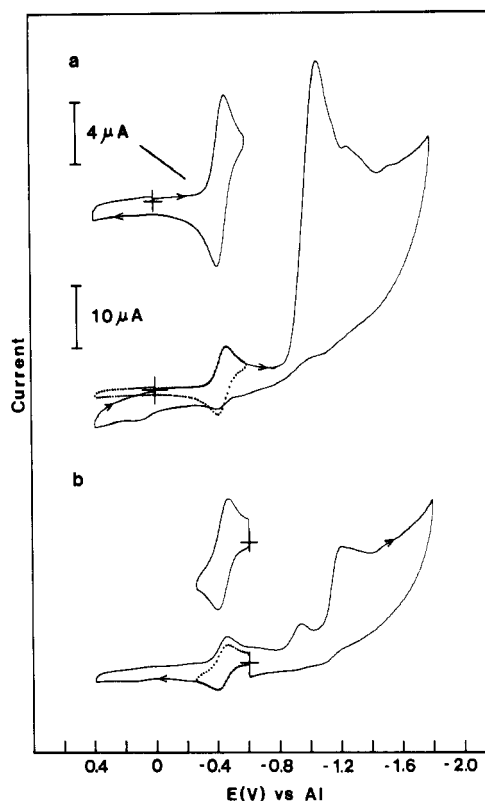


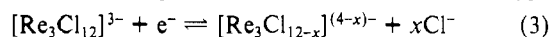
Figure 5. Cyclic voltammograms of trimeric rhenium chloride complexes at a glassy-carbon electrode in the 44.4/55.6 mol % $\text{AlCl}_3\text{-MeEtimCl}$ molten salt at 40.0 °C: (a) 3.80×10^{-3} M Re_3Cl_9 ; (b) solution in (a) after exhaustive reduction at -0.60 V (note: the current scales are the same as those in (a)). The scan rates were 50 mV s^{-1} .

Re_3Cl_9 . An absorption spectrum of a solution of Re_3Cl_9 in the 44.4/55.6 mol % $\text{AlCl}_3\text{-MeEtimCl}$ melt is illustrated in Figure 4. Wavelength and molar absorptivity data taken from this and a similar spectrum that was recorded in the 49.0/51.0 mol % melt are given in Table I. The spectral data for Re_3Cl_9 originating from the molten salt are very similar to those recorded for this compound in aqueous HCl (Figure 4 and Table I) where Re_3Cl_9 is known to be complexed as $[\text{Re}_3\text{Cl}_{12}]^{3-}$.²⁸ Thus, it appears that $[\text{Re}_3\text{Cl}_{12}]^{3-}$ is the species produced when Re_3Cl_9 is dissolved in basic $\text{AlCl}_3\text{-MeEtimCl}$. Re_3Cl_9 was found to be virtually insoluble in neutral and acidic melts.

(28) Bertrand, J. A.; Cotton, F. A.; Dollase, W. A. *Inorg. Chem.* **1963**, *2*, 1166.

A cyclic voltammogram of a solution of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ in basic melt is shown in Figure 5a. The morphology of this voltammogram is somewhat similar to that for $[\text{Re}_2\text{Cl}_8]^{2-}$ in that a small reduction wave is succeeded at more negative potentials by a much larger reduction process. Analysis of the first reduction wave appearing at $E_p = -0.47$ V in the 44.4/55.6 mol % melt and -0.37 V in the 49.0/51.0 mol % melt suggested that it, like the first oxidation wave for $[\text{Re}_2\text{Cl}_8]^{2-}$, corresponded to a one-electron, reversible charge-transfer process that was uncomplicated by homogeneous chemistry on the voltammetric time scale; i.e., ΔE_p averaged about 0.064 V, i_p^c/i_p^a was 1.0, and $i_p^c/v^{1/2}$ was essentially constant over the range of scan rates employed for these studies, 0.010–0.200 V s⁻¹. Likewise, a plot of i_L versus the square root of the angular velocity of the GCRDE was linear and passed through the origin.

Electrochemical data for the first reduction wave are collected in Table II. Examination of these data indicates that $E_{1/2}$ for the reduction of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ exhibits a much larger shift with melt composition (0.095 V/pCl unit) than $E_{1/2}$ for the reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$ and other transition-metal chloride complexes, which have been shown to retain the same chloride coordination after reduction (vide supra). A plot of $E_{1/2}$ versus pCl, which was constructed from several extensive titration experiments in which $E_{1/2}$ for the reduction of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ was recorded versus the ferrocene/ferrocenium couple as the melt composition was varied over the range of compositions from 49.6/50.4 to 39.9/60.1 mol %, was linear and exhibited a slope of 0.094 V/pCl unit. If this slope is corrected by subtracting the approximate 0.020 V/pCl unit shift that has been observed for transition-metal redox couples that preserve their coordination after reduction, then the remaining value (0.074 V/pCl unit) is reasonably close to the 0.062 V/pCl unit theoretical slope expected for a redox reaction of the type



in which $x = 1$. This dependence of $E_{1/2}$ on pCl does not come as a complete surprise because a similar pCl dependence was observed during the reduction of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ in aqueous HCl.⁹ The results observed in aqueous HCl were interpreted in terms of the loss of one terminal in-plane chloride ion on each rhenium atom in the cluster during reduction. Radiochemical exchange experiments have shown the chloride ions in this position to be quite labile.²⁹ The loss of a labile chloride ion from $[\text{Re}_3\text{Cl}_{12}]^{3-}$ during the one-electron reduction of this species, which should be a very facile process requiring essentially no structural reorganization of the complex and only a small activation energy barrier, is consistent with the reversible nature of the electrode reaction found here.

In parallel with the investigation of $[\text{Re}_2\text{Cl}_8]^{2-}$ (vide supra), we next investigated the bulk controlled-potential reduction of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ at an applied potential of -0.55 V in an effort to prepare stable solutions of its one-electron-reduction product for further study. The initial segments of plots of $\log i$ versus t that were constructed from the electrolysis current–time data gave values of $n = 1.18$ and 1.13 in separate experiments. Like the reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$, the reduction of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ was affected by trace amounts of oxygen in the glovebox atmosphere. However, the $[\text{Re}_2\text{Cl}_8]^{2-}$ reduction product appeared to be somewhat less susceptible to oxidation by trace oxygen than $[\text{Re}_2\text{Cl}_8]^{3-}$. A cyclic voltammogram of a solution of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ that was reduced as described above is shown in Figure 5b, and it can be seen that the reduction product of this species is now present in the solution. This reduced species must be the same as that observed during the voltammetric experiments, i.e., $[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$, because the average $E_{1/2}$ for the oxidation of this reduced species is experimentally indistinguishable from that for the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ one-electron reduction wave (Table II).

Solutions containing $[\text{Re}_3\text{Cl}_{12}]^{3-}$ changed from a dark red to a deep purple color upon reduction at -0.55 V. An absorption spectrum of one of these exhaustively reduced solutions is shown in Figure 4, and data taken from this spectrum are collected in

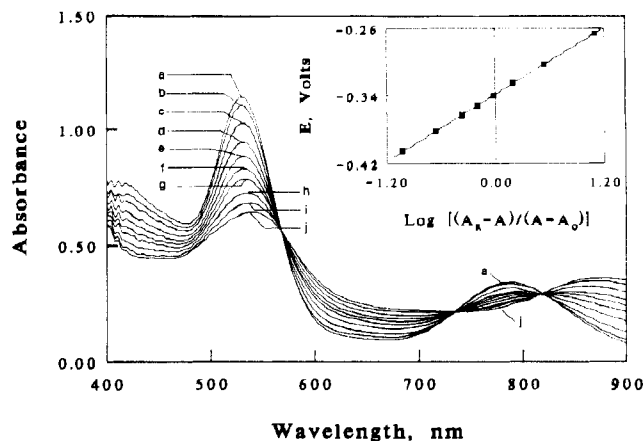


Figure 6. Absorption spectra of a 6.08×10^{-3} M solution of Re_3Cl_9 in the 49.0 mol % AlCl_3 – MeEtimCl molten salt at 40.0 °C in the RGC-OTE cell at various applied potentials (V): (a) open circuit; (b) -0.266 ; (c) -0.303 ; (d) -0.325 ; (e) -0.340 ; (f) -0.352 ; (g) -0.364 ; (h) -0.383 ; (i) -0.405 ; (j) -0.550 . Inset: Nernst plot constructed from these spectra.

Table I. Some of the more subtle changes that take place in the 400–900-nm spectral region during the reduction of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ to $[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$ can be seen more clearly in Figure 6. This figure, like Figure 3, resulted from a spectropotentiostatic experiment with the RGC-OTE cell. Data for the Nernst plot (eq 2) shown in the inset of this figure were obtained by recording the absorbance of the 530-nm band after equilibrium was established following selected potential steps. The slope of this plot is 0.066 V and is in very good agreement with the theoretical slope of 0.062 V expected for a one-electron redox couple. The $[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$ produced in the RGC-OTE cell could be converted back to $[\text{Re}_3\text{Cl}_{12}]^{3-}$ quantitatively by the application of a suitable positive potential step.

Like $[\text{Re}_2\text{Cl}_8]^{2-}$, $[\text{Re}_3\text{Cl}_{12}]^{3-}$ also exhibits a second, very large voltammetric reduction process whose current is many times greater than that observed for the one-electron reduction of this species (Figure 5a). Unfortunately, we cannot provide an explanation for this multielectron reduction process either; however, we do offer the following observations. This process may consist of a combination of two or more successive reduction waves because the current observed after the wave at -1.09 V is traversed does not exhibit the expected $t^{-1/2}$ decay. In addition, the top of a second reduction wave with an E_p of ca. -1.27 V can be seen in this figure. It was also necessary to clean the electrode surface after this large reduction process was traversed in order to remove an insoluble film that partially blocked the electrode surface. Curve crossing could be seen on the reverse scan in the potential region between the reduction waves at $E_p = -0.37$ and -1.09 V if the electrode had been freshly polished and if the scan was reversed immediately after the peak at -1.09 V was traversed. The current for the wave at $E_p = -1.09$ V did not decrease significantly relative to that for the one-electron reduction process at $E_p = -0.47$ V at fast scan rates. However, the current for the reduction wave at $E_p = -1.09$ V disappears and what appears to be a new reduction wave can be seen at $E_p = -0.95$ when all of the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ was reduced to $[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$ (Figure 5b). The height of the wave at $E_p = -0.95$ V is identical with the height of the $[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$ oxidation wave, suggesting that this new wave corresponds to a one-electron reduction process. However, this new reduction wave does not exhibit a reverse current. In addition, the wave with $E_p = -1.27$ V can be seen more clearly in these reduced solutions. These results suggest that $[\text{Re}_3\text{Cl}_{12}]^{3-}$ may be involved in a very rapid coupled homogeneous chemical step that leads ultimately to the unusual size of the wave at $E_p = -1.09$ V. As was the case for the dimer, controlled-potential electrolysis at -1.20 V, which is negative of this large wave, destroys the trimeric cluster.

Diffusion Coefficients. Diffusion coefficients, D , and Stokes–Einstein products, $\eta D/T$, where η is the absolute viscosity of the ionic solvent and T is the absolute temperature, are shown in Table

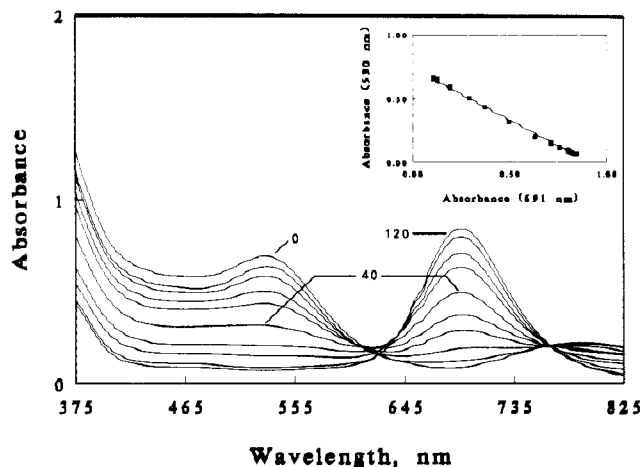


Figure 7. Absorption spectra of a 5.74×10^{-4} M solution of Re_3Cl_9 in the 49.0/51.0 mol % AlCl_3 -MeEtimCl molten salt as a function of time (min) after incubation at 185°C . The cell path length was 1.00 cm. Inset: plot of the absorbance at 530 nm versus the absorbance at 691 nm constructed from these spectra.

II for $[\text{Re}_2\text{Cl}_8]^{2-}$, $[\text{Re}_3\text{Cl}_{12}]^{3-}$, and their one-electron-reduction products. Uncertainty in the value of the constant that is to be used in the Stokes-Einstein equation for anionic transition-metal complexes in these melts precludes the possibility of directly calculating the radius of the diffusing entity from D and η with this equation. However, relative comparisons of the sizes of these diffusing complexes are still possible through comparison of their $\eta D/T$ values, which are inversely proportional to the radii of the diffusing entities. Surprisingly, the $\eta D/T$ values for $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_3\text{Cl}_{12}]^{3-}$ are very similar to those for monomeric species with the same overall charge, e.g., $[\text{IrCl}_6]^{2-}$ ($1.8 \times 10^{-10} \text{ g cm s}^{-2} \text{ K}^{-1}$),²² $[\text{NbCl}_6]^{2-}$ ($2.1 \times 10^{-10} \text{ g cm s}^{-2} \text{ K}^{-1}$),¹² $[\text{IrCl}_6]^{3-}$ ($1.3 \times 10^{-10} \text{ g cm s}^{-2} \text{ K}^{-1}$),²² and others.² Furthermore, the $\eta D/T$ values for $[\text{Re}_2\text{Cl}_8]^{3-}$ and $[\text{Re}_3\text{Cl}_{12}]^{3-}$ are virtually identical although the latter would ordinarily be expected to exhibit a smaller $\eta D/T$ by virtue of its greater physical size. These results lend further support to the supposition that the magnitude of $\eta D/T$ is more closely related to the overall charge on the complex than to the oxidation state of its metal core or to its coordination geometry.¹² Although the full implications of this correlation have not been established, these results suggest that these anionic complexes may diffuse in the melt in intimate association with MeEtim⁺ cations.

Conversion of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ to $[\text{Re}_2\text{Cl}_8]^{2-}$. Bailey and McIntyre¹¹ reported that Re_3Cl_9 is stable in molten dimethyl sulfone but converts to $[\text{Re}_2\text{Cl}_8]^{2-}$ when chloride ions are introduced into this solvent. They also found that $[\text{Re}_2\text{Cl}_8]^{2-}$ is produced when the rhenium(III) is added to this molten solvent as the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ complex. In addition, the conversion of Re_3Cl_9 to $[\text{Re}_2\text{Cl}_8]^{2-}$ in molten $[\text{C}_2\text{H}_5]_2\text{NH}_2\text{Cl}$ at 217 – 220°C forms the basis of a useful method for preparing the dimeric complex in relatively high yield.³⁰

In view of these previous results, we investigated some of the conditions that lead to the conversion of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ to $[\text{Re}_2\text{Cl}_8]^{2-}$ in basic AlCl_3 -MeEtimCl.

It was found that temperatures equal to or greater than ca. 175°C brought about the conversion of the trimer into the dimer. Figure 7 shows a series of absorption spectra that were recorded at different times during the incubation of a dilute solution of $[\text{Re}_3\text{Cl}_{12}]^{3-}$ in the 49.0/51.0 mol % melt at 185°C . After a short induction period lasting about 20 min at this temperature in which only a small amount of trimer is converted into the dimer, the conversion process proceeds much more rapidly; the disappearance of the trimeric species was essentially complete after about 1 h of total elapsed time. The inset in Figure 7 shows a plot of the absorbance of the 530-nm band for $[\text{Re}_3\text{Cl}_{12}]^{3-}$ versus the absorbance at 691-nm band for $[\text{Re}_2\text{Cl}_8]^{2-}$ that was constructed from the spectra in this figure. The slope of this plot gives information about the number of moles of the latter that are produced per mole of the former. However, in order to extract this information, the molar absorptivities, ϵ , of the unadulterated dimer and trimer in the melt at the experimental temperature must be known. This information was obtained without difficulty in the case of the dimer ($\epsilon = 1710 \text{ M}^{-1} \text{ cm}^{-1}$) because this complex was perfectly stable in the melt at 185°C . However, since small amounts of the trimer were converted to the dimer almost immediately after the cuvette reached the temperature of the furnace,³¹ it was necessary to first calculate the spectrum of the pure trimer in the melt by using the method described by Griffiths³² and to then estimate the absorptivity of the trimer ($\epsilon = 1196 \text{ M}^{-1} \text{ cm}^{-1}$) from this calculated spectrum. On the basis of these absorptivities and the experimental slope of the plot in Figure 7 (0.81), it appears that only one dimer is produced for each trimer during the conversion process; i.e., the yield of dimer is only about 67%. Similar results were obtained in the 44.4/55.6 mol % melt. This result is not surprising because an identical yield is observed during the conversion of Re_3Cl_9 to $[\text{Re}_2\text{Cl}_8]^{2-}$ in molten $[\text{C}_2\text{H}_5]_2\text{NH}_2\text{Cl}$. This also suggests that a third species is produced during the conversion process. However, we were unable to detect any obvious evidence of this species, but it is possible, that this elusive complex may account for the lack of an expected isosbestic point at ca. 625 nm in the spectra shown in Figure 7.

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(30) Brignole, A. B.; Cotton, F. A. *Inorg. Synth.* **1972**, *13*, 81.

(31) Experiments that were conducted with a miniature chromel-alumel thermocouple indicated that the cell contents reached the temperature of the furnace in less than 3 min.

(32) Griffiths, T. R. In *Molten Salt Techniques*; Gale, R. J., Lovering, D. G., Eds.; Plenum: New York, 1984; Vol. 2, Chapter 4.