molecules, it is quite conceivable that a proton could fit inside one of these cubes.[31] To examine this possibility, calculations were performed on the species $(H)H_8Si_8O_{12}^+$ where the proton was placed on the inside of the cube. A stationary point was found where the proton was attached to a bridging oxygen atom that had distorted such that it was pointing inside of the cube also. This type of distortion would be expected since the bridging oxygen atoms in these molecules bend away from the center of the Si_8O_{12} core, which should force the bridging oxygen electron lone pairs to be oriented away from the core. However, a force calculation on this distorted geometry yielded a single negative eigenvalue, which indicates that this was a transition state and not a true ground state.[21] This transition state was calculated to lie about 8 kcal/mol higher in energy than the minima found where protonation occurred on the outside of the cube.

Conclusion

This work has shown that semiempirical calculations can be successfully applied to molecular aluminosilicates to predict geometries and relative stabilities of geometric isomers. While the calculated Si–O bond lengths are consistently longer than the experimental values, the errors were found to be reasonably constant (ca. +0.10 Å) and size-independent, which allows even rather subtle trends to be successfully predicted. The relative stability of geometric isomers of the general formula $R_8Al_xSi_{8-x}O_{12}^{x-}$ were calculated and found to be in agreement with Loewenstein's rule, suggesting that these systems may be used to successfully study certain properties of zeolites. Protonation studies on these molecules suggest, as expected, that protonation occurs preferentially at bridging oxygen atoms adjacent to aluminum. Further studies are currently in progress to model organic transformations on these molecules and to examine larger systems.

Supplementary Material Available: Complete tables of Cartesian coordinates at the optimized geometries and calculated atomic charges for all molecules included in this study (34 pages). Ordering information is given on any current masthead page.

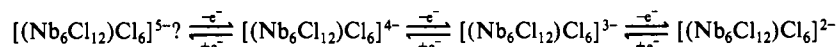(31) The body diagonal of these cubes is ca. 5.3 Å.

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Electrochemical and Spectroscopic Characterization of {Nb6Cl12}^z+ Chloride Clusters in the Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Molten Salt

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The electrochemistry and electronic absorption spectroscopy of metal-metal-bonded chloride clusters derived from the {Nb6Cl12}^z+ (z = 1–4) cores were investigated in the room-temperature molten salt aluminum(III) chloride–1-methyl-3-ethylimidazolium chloride (AlCl3–MeEtimCl). Anionic complexes of this core cluster of the type [(Nb6Cl12)Cl6]^{(6-z)-} were identified in basic melt. Reversible electrode reactions with $E_{1/2}$ values of –0.02 and 0.39 V versus the Al^{3+}/Al couple in the 66.7/33.3 mol % AlCl3–MeEtimCl melt at 100 °C were found for the oxidation of the chloride complexes derived from the {Nb6Cl12}^{2+} and {Nb6Cl12}^{3+} cores, respectively. The overall redox scheme for these complexes is

$$[(Nb_6Cl_{12})Cl_6]^{5-}? \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(Nb_6Cl_{12})Cl_6]^{4-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(Nb_6Cl_{12})Cl_6]^{3-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(Nb_6Cl_{12})Cl_6]^{2-}$$

[(Nb6Cl12)Cl6]^{5-} is moderately stable on the voltammetric time scale but decomposes during controlled-potential electrolytic reduction of the parent species. Likewise, [(Nb6Cl12)Cl6]^{2-} is voltammetrically stable, but bulk solutions of this complex are slowly reduced to [(Nb6Cl12)Cl6]^{3-} by chloride ion in basic melt. Reversible electrochemical reactions involving the {Nb6Cl12}^{2+/3+} and {Nb6Cl12}^{3+/4+} redox systems were also found in acidic melt at 1.13 and 1.50 V, respectively, and solutes containing the {Nb6Cl12}^z+ (z = 2–4) cores exhibited long-term stability. The approximate 1-V positive shift in the $E_{1/2}$ values for these redox reactions in acidic melt relative to the $E_{1/2}$ values found in basic melt suggests that as many as six of the labile chloride ions that are associated with the [(Nb6Cl12)Cl6]^{(6-z)-} clusters in basic melt may be replaced by [AlCl4]^- ions when these clusters are dissolved in acidic melt. The Stokes–Einstein products of the niobium clusters in both acidic and basic melts are essentially independent of the oxidation level of the core. The average values of these products are 8.2×10^{-11} (40 °C) and 1.2×10^{-10} (100 °C) g cm s^{-2} K^{-1}, respectively.

Introduction

The combination of aluminum(III) chloride and certain quaternary organic chloride salts with "bulky" cations, notably 1-(1-butyl)pyridinium chloride (BupyCl) and 1-methyl-3-ethylimidazolium chloride (MeEtimCl), results in ionic liquids or molten salts that are fluids at room temperature. Several reviews covering various aspects of these room-temperature chloroaluminate melts are available.[4] The Lewis acidity of these molten salts can be varied over a large range by simply altering the AlCl3 content of the mixture. This adjustable acidity leads to a family of solvents with vastly different properties. For example, mixtures that are greater than 50 mol % in AlCl3 are Lewis acidic due to the presence of powerful chloride ion acceptors like [Al2Cl7]^- and [Al3Cl10]^- whereas those melts that are less than 50 mol % in AlCl3 are Lewis basic because they contain chloride ion that is not covalently bound to aluminum.

Basic room-temperature chloroaluminate melts are excellent solvents for transition metal chloride complexes,[5] including the chloride complexes of heteropolyatomic transition metal clusters. The electrochemistry and electronic absorption spectroscopy of several of these clusters have been investigated in these ionic solvents. Among the species that have been studied to date are [Mo2Cl8]^{4-},[6] [(Mo6Cl8)Cl6]^{2-},[7] [Re2Cl8]^{2-},[8] [Re2Cl8]^{3-},[9] [Re2-

(1) University of Sussex.
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(4) Reviews: (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. In *Advances in Molten Salt Chemistry*; Mamantov, G., Mamantov, C. B., Eds.; Elsevier: Amsterdam, 1983; Vol. 5, pp 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.

(5) (a) Appleby, D.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Nature* **1986**, *323*, 614. (b) Hussey, C. L. *Pure Appl. Chem.* **1988**, *60*, 1763.
(6) Carlin, R. T.; Osteryoung, R. A. *Inorg. Chem.* **1988**, *27*, 1482.
(7) Barnard, P. A.; Sun, I-W.; Hussey, C. L. *Inorg. Chem.* **1990**, *29*, 3670.
(8) Strubinger, S. K. D.; Sun, I-W.; Cleland, W. E.; Hussey, C. L. *Inorg. Chem.* **1990**, *29*, 993.

$Cl_9]^-$,[10] $[Re_3Cl_{12}]^{3-}$,[8] and $[W_2Cl_9]^{3-}$.[11] As part of a continuing investigation into the chemistry of these unusual metal-metal-bonded species in room-temperature chloroaluminates, we report herein electrochemical and spectroscopic investigations of the niobium chloride clusters derived from the dodecakis(μ-chloro)-hexaniobium(z+) core, $\{Nb_6Cl_{12}\}^{z+}$ (z = 1–4) in both acidic and basic AlCl$_3$–MeEtimCl melts. Structurally, the six niobium atoms that comprise the $\{Nb_6Cl_{12}\}^{z+}$ core cluster are arranged in the shape of an octahedron with each niobium atom joined to four others through metal-metal bonds with a formal bond order of $^2/_3$.[12] Each of the twelve chlorine atoms in the core cluster bridges two niobium atoms along a unique edge of the metal octahedron. Six relatively labile chlorides can be added to the core cluster in terminal positions along the axes of the metal octahedron to produce anionic chloride complexes of the general type $[(Nb_6Cl_{12})Cl_6]^{(6-z)-}$.

For the most part, the electrochemistry of well-defined clusters derived from the $\{Nb_6Cl_{12}\}^{2+}$ core, especially those possessing only chloride ligands, has not been characterized with modern techniques. The electrochemistry of such species was first studied by McCarley et al.,[13] who examined the polarographic oxidation of $Nb_6Cl_{14}\cdot7H_2O$ in aqueous 1 M KClO$_4$ at a dropping mercury electrode (DME). A single oxidation wave with a half-wave potential, $E_{1/2}$, of 0.426 V versus the saturated calomel electrode (SCE) was found and was attributed to the two-electron oxidation of $\{Nb_6Cl_{12}\}^{2+}$ to $\{Nb_6Cl_{12}\}^{4+}$. Somewhat later, Mackay and Schneider[14] conducted polarographic studies in dimethyl sulfoxide (DMSO) solutions containing either $[(Nb_6Cl_{12})Cl_6]^{2-}$ or $[(Nb_6Cl_{12})Cl_6]^{3-}$, and they found that each complex produced two waves of equal height appearing at $E_{1/2}$ = –0.10 and 0.70 V versus SCE. More recently, Klendworth and Walton[15a] explored the electrochemistry of the related tertiary phosphine complexes containing the $\{Nb_6Cl_{12}\}^{2+}$ core at a platinum bead electrode in dichloromethane. The cyclic voltammetry of these complexes, represented here as $[(Nb_6Cl_{12})Cl_2(PR_3)_4]$ (R_3 = Et$_3$, n-Pr$_3$, Et$_2$Ph), revealed two successive one-electron quasireversible oxidation waves and a single one-electron quasireversible reduction wave with $E_{1/2}$ values of 0.53, 1.09, and ca. –0.99 V versus SCE, respectively. These waves were attributed to the following electrode processes

$$[(Nb_6Cl_{12})Cl_2(PR_3)_4]^- \underset{+e^-}{\overset{-e^-}{\rightleftarrows}} [(Nb_6Cl_{12})Cl_2(PR_3)_4] \underset{+e^-}{\overset{-e^-}{\rightleftarrows}}$$

$$[(Nb_6Cl_{12})Cl_2(PR_3)_4]^+ \underset{+e^-}{\overset{-e^-}{\rightleftarrows}} [(Nb_6Cl_{12})Cl_2(PR_3)_4]^{2+} \quad (1)$$
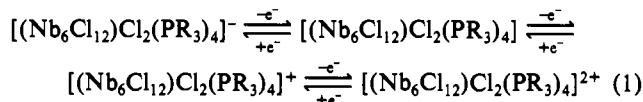
The $E_{1/2}$ values of these reactions were independent of the type of phosphine ligands that were employed, within the limited subset of compounds studied. Penicaud et al.[15b] reported a voltammetric oxidation wave with $E_{1/2}$ = 1.72 V versus SCE in acetonitrile solutions containing $[(Nb_6Cl_{12})Cl_6]^{3-}$ that they attributed to the generation of a complex species derived from the 13-electron core cluster $\{Nb_6Cl_{12}\}^{5+}$.

Only a few very limited studies involving niobium clusters have been undertaken in chloride-based molten salts. The reduction of NbCl$_5$ in AlCl$_3$–NaCl(satd) at 160 °C is reported to produce a trimeric cluster containing the $\{Nb_3\}^{8+}$ core,[16] but no information was given about the chloride coordination of this species. Masse and Simon[17] reported that solid $K_4[(Nb_6Cl_{12})Cl_6]$ is obtained at

a graphite cathode when Nb$_3$Cl$_8$ is oxidized at a niobium anode in molten LiCl–KCl eutectic at 610 °C. However, insofar as we can determine, no detailed electrochemical or spectroscopic investigations of species derived from the $\{Nb_6Cl_{12}\}^{z+}$ core have been undertaken in chloroaluminate molten salts.

Experimental Section

Apparatus. All electrochemical experiments were performed in a dry, oxygen-free nitrogen atmosphere inside a Kewaunee Scientific Equipment Corp. (KSE) glovebox system. This glovebox system is equipped with a KSE Model 2C2500 30 ft^3 min^{-1} inert-gas purification system. The quality of the atmosphere inside the glovebox was monitored with a lighted Phillips 25-W, 115-V CL/VS incandescent light bulb with a hole pierced in the glass envelope. A filament life of ca. 10 days was associated with a combined oxygen and moisture content of less than 1 ppm.[18]

Cyclic and rotating disk electrode (RDE) voltammetry, chronoamperometry, and controlled-potential electrolysis were carried out with an EG&G Princeton Applied Research Corp. (PARC) Model 173 potentiostat, PARC Model 179 digital coulometer plug-in module, and PARC Model 175 universal programmer. Controlled electrode rotation was provided by a Pine Model AFASR electrode rotator. Electrochemical data were displayed on a Houston Instruments Model 100 X-Y/Y-t recorder and/or a Hewlett-Packard 3467A logging multimeter. The electrochemical cell, furnace used to heat the cell, Pyrex glass/glassy carbon disk working electrode (geometrical surface area = 0.0707 cm^2) that is designed for use at elevated temperatures, and reference and counter electrodes were described at length in a previous publication.[11] Bulk controlled-potential electrolysis was carried out at either a large surface area platinum basket or a glassy carbon cup working electrode. The reference electrode was the Al^{3+}/Al couple in 66.7/33.3 mol % AlCl$_3$–MeEtimCl. The potential reproducibility of this electrode is ca. ± 10 mV, as determined from extensive measurements with ferrocene. Electronic resistance compensation was employed during all electrochemical experiments except controlled-potential electrolysis.

Spectroelectrochemical experiments were carried out directly in the glovebox with a computer-interfaced, fiber optic spectrophotometry system and a cell with a reticulated glassy carbon optically transparent electrode (RGC-OTE).[19] Electronic spectra were recorded in bulk melts outside the glovebox in 1.0 mm path length fused silica cells fitted with gastight Teflon caps by using a Perkin-Elmer Model 3840 Lambda Array spectrophotometer operating in the high-performance mode or with a Perkin-Elmer Hitachi 200 UV–vis spectrophotometer.

Chemicals. Aluminum(III) chloride (Fluka, >99%) was sublimed under vacuum inside a glovebox a minimum of three times before use. The first sublimation was carried out from AlCl$_3$–NaCl melt. The procedures used to synthesize and purify MeEtimCl were identical to those reported by Wilkes et al.[20] (Nb$_6$Cl$_{12}$)Cl$_2$·8H$_2$O was prepared under nitrogen by following the method of Koknat et al.[21] This compound was used as the starting material for the preparation of the salts [MeEtim]$_3$[(Nb$_6$Cl$_{12}$)Cl$_6$] and [MeEtim]$_2$[(Nb$_6$Cl$_{12}$)Cl$_6$]. The complete details of the synthesis of these salts and some related clusters, along with the full crystal structures of these compounds, will be reported separately.[22] At the outset of the study reported herein, we found that these compounds were sometimes contaminated by varying amounts (usually <2 % w/w) of an intractable niobium(V) oxide chloride compound whose voltammetric characteristics in basic melt were identical to those of [NbOCl$_5$]$^{2-}$.[23] We speculate that this contaminant is NbOCl$_3$, which is converted to this anionic complex when the impure cluster compound is dissolved in basic melt. When necessary, the cluster concentration in solution was corrected for the presence of this contaminant; the amount of NbOCl$_3$ in the synthesized cluster compound was estimated from the [NbOCl$_5$]$^{2-}$ reduction current and diffusion coefficient.

Results and Discussion

The $\{Nb_6Cl_{12}\}^{2+}$ core was used as the initial oxidation level for all of the electrochemical and spectroscopic studies described herein. This core was chosen as the starting point because pre-

(9) Strubinger, S. K. D.; Hussey, C. L.; Cleland, W. E. *Inorg. Chem.* **1991**, *30*, 4276.

(10) Strubinger, S. K. D.; Sun, I-W.; Cleland, W. E.; Hussey, C. L. *Inorg. Chem.* **1990**, *29*, 4246.

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

(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1079.

(13) McCarley, R. E.; Hughes, B. G.; Cotton, F. A.; Zimmerman, R. *Inorg. Chem.* **1965**, *4*, 1491.

(14) Mackay, R. A.; Schneider, R. F. *Inorg. Chem.* **1967**, *6*, 549.

(15) (a) Klendworth, D. D.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 1151. (b) Penicaud, A.; Batail, P.; Coulon, C.; Canadell, E.; Perrin, C. *Chem. Mater.* **1990**, *2*, 123.

(16) Ting, G.; Fung, K. W.; Mamantov, G. *J. Electrochem. Soc.* **1976**, *123*, 624.

(17) Masse, R.; Simon, A. *Mater. Res. Bull.* **1981**, *16*, 1007.

(18) Foust, R. A. *General Motors Research Bulletin*; General Motors: Detroit, MI, Oct 3, 1968.

(19) (a) Ward, E. H.; Hussey, C. L. *Anal. Chem.* **1986**, *59*, 213. (b) Ward, E. H.; Barnard, P. A.; Sun, I-W.; Hussey, C. L. *Proc.—Electrochem. Soc.* **1987**, *87-7*, 445.

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

(21) Koknat, F. W.; McCarley, R. E. *Inorg. Chem.* **1974**, *13*, 295.

(22) Hitchcock, P. B.; Quigley, R.; Seddon, K. R. To be submitted for publication.

(23) Sun, I-W.; Hussey, C. L. *Inorg. Chem.* **1989**, *28*, 2731.
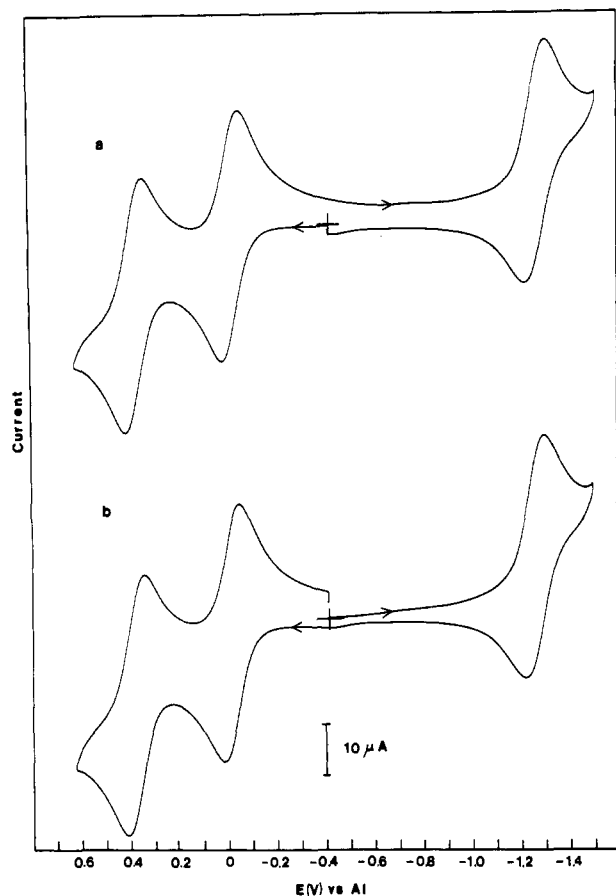
Figure 1. Cyclic voltammograms of 7.05 mM [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ at a glassy carbon electrode in the 49.0/51.0 mol % AlCl$_3$–MeEtimCl molten salt at 100 °C: (a) scan toward negative potentials; (b) scan toward positive potentials. This solution was prepared by dissolving [MeEtim]$_3$[(Nb$_6$Cl$_{12}$)Cl$_6$] and then reducing the complex ion to [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ at –0.40 V. The scan rates were 50 mV s^{-1}, and the initial potential for each scan was –0.40 V.

liminary studies suggested that clusters derived from cores with higher oxidation levels might be unstable; i.e., they may oxidize a component of the ionic solvent, probably chloride ion. Additional studies subsequently revealed that this was true only for clusters containing the {Nb$_6$Cl$_{12}$}$^{4+}$ core in basic melt solutions (vide infra). Cluster species containing the {Nb$_6$Cl$_{12}$}$^{2+}$ core were introduced into the melt via several different routes, e.g., by dissolving (Nb$_6$Cl$_{12}$)Cl$_2$·8H$_2$O or by dissolution of the [MeEtim]$_3$-[(Nb$_6$Cl$_{12}$)Cl$_6$] and [MeEtim]$_2$[(Nb$_6$Cl$_{12}$)Cl$_6$] salts. However, it was necessary to adjust the oxidation level of the cluster in solution by employing controlled-potential electrolysis when the latter two compounds were used. This latter approach was preferred because both of the imidazolium salts dissolved fully after only a few hours of heating and stirring, whereas complete dissolution of the hydrated material usually required vigorous stirring for several days at high temperature.

Basic Melts. The solubility of the aforementioned compounds in basic melt at room temperature was ca. 1 mM. This solubility level was more than sufficient to permit the recording of spectral data; however, solutions with higher concentrations of cluster were required in order to collect well-resolved voltammograms that were free from the distortion due to background currents. Therefore, it was necessary to conduct electrochemical experiments at elevated temperatures, and a temperature of 100 °C was arbitrarily chosen. However, the solubility of the various cluster compounds at this temperature was still very low, ca. 5–10 mM at best.

Cyclic voltammograms at a glassy carbon electrode of a solution of [MeEtim]$_3$[(Nb$_6$Cl$_{12}$)Cl$_6$] in basic melt that was exhaustively reduced at –0.40 V are shown in Figure 1. The voltammogram initiated toward more positive potentials reveals the presence of oxidation waves with peak potentials, E_p, at ca. 0.01 and 0.41 V,
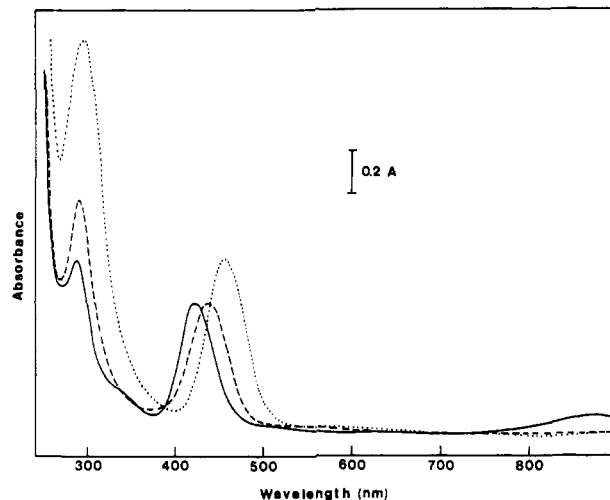
Figure 2. Absorption spectra of niobium chloride clusters in the 44.4/55.6 mol % melt at room temperature: (—) 0.480 mM solution of [MeEtim]$_3$[(Nb$_6$Cl$_{12}$)Cl$_6$] after reduction at –0.40 V; (- - -) foregoing solution after oxidation at 0.25 V; (···) 0.573 mM solution of (Nb$_6$-Cl$_{12}$)Cl$_2$·8H$_2$O after oxidation at 0.56 V. The cell path lengths were 1.00 mm.

whereas that initiated toward less positive potentials (Figure 1b) reveals a single reduction wave with E_p = –1.30 V on the forward scan. All of these waves exhibit reverse currents. Identical voltammograms were obtained for a solution prepared with [MeEtim]$_2$[(Nb$_6$Cl$_{12}$)Cl$_6$] that was pretreated in the same fashion, i.e., by exhaustive reduction at –0.40 V. Overall, the cyclic voltammograms in Figure 1 exhibit very close resemblance to those obtained for some other classes of complex species derived from the {Nb$_6$Cl$_{12}$}$^{2+}$ core cluster, e.g., the [(Nb$_6$Cl$_{12}$)Cl$_2$(PR$_3$)$_4$] complexes in dichloromethane[15a] (eq 1).

An electronic absorption spectrum of a very dilute solution of [MeEtim]$_3$[(Nb$_6$Cl$_{12}$)Cl$_6$] in basic melt that was prepared in the same fashion as that used for voltammetry (vide supra) is shown in Figure 2. Data taken from this spectrum are collected in Table I along with spectral data for the [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ chloride complex in ethanol (EtOH) and EtOH saturated with HCl. No attempt was made to document the very weak absorption bands appearing in the melt spectrum or to calculate the molar absorptivities of shoulders. Although there is more variability in the literature data, especially with regard to molar absorptivities, the major features of the spectrum shown in Figure 2 nevertheless compare favorably with the literature data, strongly suggesting that this chloride complex is the electroactive species present in basic AlCl$_3$–MeEtimCl under these conditions. Virtually identical spectral data were obtained with basic melt solutions prepared by the direct introduction of the {Nb$_6$Cl$_{12}$}$^{2+}$ core, i.e., by dissolution of (Nb$_6$Cl$_{12}$)Cl$_2$·8H$_2$O.

As noted above, [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ exhibits two oxidation waves and a single reduction wave. In a typical experiment, the peak potential for the first oxidation wave was independent of scan rate, and the peak potential separation, ΔE_p, for the first oxidation wave and its associated reduction wave averaged 0.073 V over the range of scan rates extending from 0.010 to 0.200 V s^{-1}. This value is in excellent agreement with the 0.074-V separation expected for a one-electron reversible (mass-transport-controlled) electrode reaction at 100 °C. In addition, the peak current ratio, estimated by using Nicholson's empirical equation,[26] was 1.0, and the peak current function, $i_p/v^{1/2}$, was constant over this same range of scan rates, indicating the absence of coupled homogeneous chemistry. This oxidation process was also investigated by using RDE voltammetry. A plot of log [($i_l - i$)/i] versus E was constructed from current–potential data taken from the descending portion of the

(24) Fleming, P. B.; McCarley, R. E. *Inorg. Chem.* **1970**, *9*, 1347.
(25) Fleming, P. B.; Dougherty, T. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 159.
(26) Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406.

Table I. Electronic Absorption Spectroscopic Data for Hexameric Niobium Clusters

solute	solvent	λ, nm (ε, M⁻¹ cm⁻¹)	ref
		$\{Nb_6Cl_{12}\}^{2+}$ Core	
[MeEtim]₃[(Nb₆Cl₁₂)Cl₆][a]	44.4/55.6 mol % AlCl₃–MeEtimCl	288 (1.7 × 10⁴), ~335,[b] 423 (1.3 × 10⁴), ~880 (1.8 × 10³)	this work
[MeEtim]₃[(Nb₆Cl₁₂)Cl₆][c]	60.0/40.0 mol % AlCl₃–MeEtimCl	297 (6.7 × 10³), ~325,[b] 394 (6.3 × 10³), ~465 w,[b] ~560 w, 865 (2.8 × 10³)	this work
[Et₄N]₄[(Nb₆Cl₁₂)Cl₆]	EtOH	214 (8.3 × 10⁴), 230,[b] 282 (1.6 × 10⁴), 325,[b] 405 (1.2 × 10⁴), 505,[b] 588,[b] 926 (4.3 × 10³)	14
[(Nb₆Cl₁₂)Cl₆]⁴⁻[d]	EtOH–HCl (satd)/Li₄[(Nb₆Cl₁₂)Cl₆]–Me₂O	214 (4.8 × 10⁴), 234 (2.7 × 10⁴), 282 (1.0 × 10⁴), 332 (3.1 × 10³), 418 (1.0 × 10⁴), 493 (1.1 × 10³), 595 (5.7 × 10²), 887 (2.1 × 10³), 998 (1.8 × 10³)	24
[(Nb₆Cl₁₂)Cl₂(P-n-Pr₃)₄]	CH₂Cl₂	260,[b] 330,[b] 412, ~610, 948	15a
		$\{Nb_6Cl_{12}\}^{3+}$ Core	
[MeEtim]₃[(Nb₆Cl₁₂)Cl₆]	44.4/55.6 mol % AlCl₃–MeEtimCl	292 (2.2 × 10⁴), 437 (1.3 × 10⁴), ~545 w, >900	this work
[MeEtim]₃[(Nb₆Cl₁₂)Cl₆]	60.0/40.0 mol % AlCl₃–MeEtimCl	279 (1.1 × 10⁴), 340,[b] 406 (7.2 × 10³), ~490,[b] ~590,[b] 800 (7.6 × 10²)	this work
[Et₄N]₃[(Nb₆Cl₁₂)Cl₆]	EtOH	218, 230,[b] 288, 426, 549,[b] 962	14
[Et₄N]₃[(Nb₆Cl₁₂)Cl₆]	MeOH	218, 289, 435, ~970	25
[(Nb₆Cl₁₂)Cl₆]³⁻[d]	EtOH–HCl(satd)	216 (4.3 × 10⁴), 233 (7.9 × 10⁴), 285 (2.0 × 10⁴), 356 (1.8 × 10³), 439 (7.4 × 10³), 538 (6.9 × 10²), 645 (2.7 × 10²), 1007 (1.5 × 10³), 1215 (1.3 × 10³), 1397 (1.1 × 10³)	24
[(Nb₆Cl₁₂)Cl₂(P-n-Pr₃)₄][PF₆]	CH₂Cl₂	~255,[b] ~300,[b] 426, 845,[b] 955, 1275	15a
		$\{Nb_6Cl_{12}\}^{4+}$ Core	
(Nb₆Cl₁₂)Cl₂·8H₂O[e]	44.4/55.6 mol % AlCl₃–MeEtimCl	297 (3.2 × 10⁴), 458 (1.5 × 10⁴), >900	this work
[MeEtim]₃[(Nb₆Cl₁₂)Cl₆][f]	60.0/40.0 mol % AlCl₃–MeEtimCl	~290,[b] 424 (8.3 × 10³), 740 (3.8 × 10²)	this work
[Et₄N]₂[(Nb₆Cl₁₂)Cl₆]	EtOH	219, 234,[b] 297, 452, 571,[b] 935	14
[(Nb₆Cl₁₂)Cl₆]²⁻[d]	EtOH–HCl(satd)	216 (4.5 × 10⁴), 234 (8.4 × 10⁴), 256 (2.0 × 10⁴), 300 (2.7 × 10⁴), 365 (3.9 × 10³), 457 (1.4 × 10⁴), 562 (6.5 × 10²), 658 (5.6 × 10²), 946 (9.4 × 10²), 1156 (1.5 × 10²)	24
[Et₄N]₂[(Nb₆Cl₁₂)Cl₆]	MeOH	234, 298, 454, ~925	25

[a] After exhaustive reduction to [(Nb₆Cl₁₂)Cl₆]⁴⁻ at −0.40 V. [b] Shoulder. [c] After exhaustive reduction to the {Nb₆Cl₁₂}²⁺ core at 0.90 V. [d] Prepared by dissolution of (Nb₆Cl₁₂)Cl₂·8H₂O in EtOH–HCl(satd); the [(Nb₆Cl₁₂)Cl₆]³⁻ and [(Nb₆Cl₁₂)Cl₆]²⁻ complexes were generated by O₂ and Cl₂ oxidation, respectively, of this solution. [e] After exhaustive oxidation of the resulting [(Nb₆Cl₁₂)Cl₆]⁴⁻ to [(Nb₆Cl₁₂)Cl₆]²⁻ at 0.56 V. [f] After exhaustive oxidation of the {Nb₆Cl₁₂}³⁺ core to the {Nb₆Cl₁₂}⁴⁺ core at 1.70 V. w = very weak.

Table II. Summary of Electrochemical Data for Hexameric Niobium Clusters in AlCl₃–MeEtimCl Melts

solute	redox syst	mol % AlCl₃	T, °C	$E_{1/2}$,[a] V	$10^7 D$,[a] cm² s⁻¹	$10^{10} \eta D/T$, g cm s⁻² K⁻¹
[(Nb₆Cl₁₂)Cl₆]⁴⁻	{Nb₆Cl₁₂}²⁺/³⁺	44.4	100	−0.020	7.13	1.1 ± 0.1
[(Nb₆Cl₁₂)Cl₆]³⁻	{Nb₆Cl₁₂}³⁺/²⁺	44.4	100	−0.020	7.01	1.1 ± 0.1
[(Nb₆Cl₁₂)Cl₆]³⁻	{Nb₆Cl₁₂}³⁺/⁴⁺	44.4	100	0.391	8.04	1.3 ± 0.1
[(Nb₆Cl₁₂)Cl₆]⁴⁻	{Nb₆Cl₁₂}²⁺/³⁺	49.0	100	−0.017	9.30	1.1 ± 0.1
[(Nb₆Cl₁₂)Cl₆]³⁻	{Nb₆Cl₁₂}³⁺/²⁺	49.0	100	−0.012	9.74	1.2 ± 0.1
[(Nb₆Cl₁₂)Cl₆]³⁻	{Nb₆Cl₁₂}³⁺/⁴⁺	49.0	100	0.389	9.94	1.2 ● 0.2
[(Nb₆Cl₁₂)Cl₆]⁴⁻	{Nb₆Cl₁₂}²⁺/¹⁺	49.0	100	−1.280	8.78	1.1 ± 0.1
[(Nb₆Cl₁₂)Clₓ(AlCl₄)₆₋ₓ]⁴⁻	{Nb₆Cl₁₂}²⁺/³⁺	60.0	40.0	1.135	2.24	0.76 ± 0.06
[(Nb₆Cl₁₂)Clₓ(AlCl₄)₆₋ₓ]³⁻	{Nb₆Cl₁₂}³⁺/²⁺	60.0	40.0	1.137	2.51	0.85 ± 0.04
[(Nb₆Cl₁₂)Clₓ(AlCl₄)₆₋ₓ]³⁻	{Nb₆Cl₁₂}³⁺/⁴⁺	60.0	40.0	1.489	2.54	0.86 ± 0.06
[(Nb₆Cl₁₂)Clₓ(AlCl₄)₆₋ₓ]²⁻	{Nb₆Cl₁₂}⁴⁺/³⁺	60.0	40.0	1.496	2.23	0.76 ● 0.13

[a] Average value from cyclic and rotating electrode voltammetry.

first oxidation wave. This plot was linear, and a value of $n = 1.0$ was calculated from the slope of this plot.

The oxidation of [(Nb₆Cl₁₂)Cl₆]⁴⁻ was also investigated with controlled-potential coulometry at an applied potential of ca. 0.25 V. Several experiments were conducted, and the average value of n resulting from four independent experiments was 0.99 ± 0.12, indicating virtually complete conversion of the {Nb₆Cl₁₂}²⁺ core to the {Nb₆Cl₁₂}³⁺ core. A cyclic voltammogram of the resulting solution was identical to that obtained for a solution prepared directly from [MeEtim]₃[(Nb₆Cl₁₂)Cl₆], and it was very similar in appearance to those shown in Figure 1, except that the rest potential was proximate to 0.25 V. No unanticipated or extraneous voltammetric waves appeared in the solution after electrolysis, and the solution was stable for at least 1 week. Furthermore, voltammetric waves for the reduction of the electrolysis product yielded an $E_{1/2}$ value that was in very good agreement with $E_{1/2}$ for the oxidation of [(Nb₆Cl₁₂)Cl₆]⁴⁻ (Table II). An absorption

spectrum of a typical oxidized solution is shown in Figure 2, and data derived from this spectrum are collected in Table I. Like the electrochemical data, the spectral data were identical to those obtained from a solution prepared directly from [MeEtim]₃-[(Nb₆Cl₁₂)Cl₆]. The spectral changes associated with the oxidation of [(Nb₆Cl₁₂)Cl₆]⁴⁻ to [(Nb₆Cl₁₂)Cl₆]³⁻ in this ionic solvent are subtle; the principal differences are shifts in the positions of the 288- and 423-nm bands associated with the latter complex to 291 and 437 nm in the oxidized complex. However, the small positional shift of the 288-nm band is accompanied by a significant increase in molar absorptivity. It was possible to quantitatively convert [(Nb₆Cl₁₂)Cl₆]³⁻ back to [(Nb₆Cl₁₂)Cl₆]⁴⁻ by reversing the electrolysis, i.e., by applying a potential of −0.40 V.

The oxidation of [(Nb₆Cl₁₂)Cl₆]³⁻ was studied with voltammetry, controlled-potential electrolysis, and absorption spectroscopy. The [(Nb₆Cl₁₂)Cl₆]³⁻ oxidation wave, which corresponds to the second oxidation wave seen for [(Nb₆Cl₁₂)Cl₆]⁴⁻ in Figure

1, also displayed the typical characteristics of a reversible electrode process that produces a stable product. For example, in a representative experiment at 100 °C, the average value of ΔE_p was 0.074 V, E_p and $i_p/v^{1/2}$ were independent of scan rate, and the peak current ratio was close to 1.0 over the same range of scan rates previously employed. Likewise, an RDE wave for this oxidation process yielded a plot of log $[(i_1 - i)/i]$ versus E that was linear with a slope corresponding to n = 0.97. The shift in $E_{1/2}$ with melt composition for the $[(Nb_6Cl_{12})Cl_6]^{3-}$ oxidation process is very small (Table II), ca. 0.003 V/pCl unit, suggesting that the chloride coordination is preserved upon oxidation.[27] Together, these data indicate that the $[(Nb_6Cl_{12})Cl_6]^{3-}$ oxidation process is a one-electron, reversible process. Furthermore, $[(Nb_6Cl_{12})Cl_6]^{2-}$ is the likely product of this electrode reaction, and it appears to be stable on the time scale of voltammetry.

Several approaches were explored in an effort to produce bulk solutions containing this complex ion. The direct introduction of this complex into basic melt through the addition of salts like $[MeEtim]_2[(Nb_6Cl_{12})Cl_6]$ produces a solution with a rest potential less positive than expected but more positive than found for a solution known to contain only $[(Nb_6Cl_{12})Cl_6]^{3-}$, suggesting that the added $[(Nb_6Cl_{12})Cl_6]^{2-}$ is partially reduced to $[(Nb_6Cl_{12})Cl_6]^{3-}$ through a homogeneous reaction with a component of the melt, probably chloride ion, upon dissolution. Controlled-potential electrolysis experiments conducted at applied potentials of 0.40 and 0.60 V at 100 °C with bulk solutions initially containing $[(Nb_6Cl_{12})Cl_6]^{3-}$ were equally unsuccessful. The electrolysis current decayed to a small steady-state value, and RDE voltammetry indicated that about 90% of this complex had been oxidized. However, when the applied potential was discontinued, much of the electrolytically produced $[(Nb_6Cl_{12})Cl_6]^{2-}$ appeared to revert back to $[(Nb_6Cl_{12})Cl_6]^{3-}$ within a few hours. A similar electrolysis experiment was conducted at room temperature ($\sim$19–20 °C) at an applied potential of 0.56 V with a very dilute solution ($<$1 mM) initially containing only $[(Nb_6Cl_{12})Cl_6]^{4-}$. In this case, after prolonged electrolysis, it appeared that virtually all of the starting material had been oxidized. A spectrum of this solution recorded immediately at the conclusion of the electrolysis experiment is shown in Figure 2. The spectral data taken from this figure agree well with literature data for the $[(Nb_6Cl_{12})Cl_6]^{2-}$ ion. However, in light of the demonstrated instability of this complex in basic melt, the molar absorptivities reported herein are only approximate.

A simple spectroelectrochemistry experiment was also undertaken with a fresh portion of this same solution in order to further probe the spectral changes taking place during the controlled-potential oxidation of $[(Nb_6Cl_{12})Cl_6]^{4-}$. This experiment was performed by advancing the potential of the RGO-OTE from −0.30 to +0.60 V in a series of small steps while the absorption spectrum was monitored in the 380–500-nm region. The current was allowed to decay to the background level following each step. Absorption spectra resulting from this experiment are shown in Figure 3. As the positive charge on the core cluster is increased, the moderately intense band at 423 nm (Table I), which has been attributed to a fully allowed metal–metal electronic transition,[24] shifts to lower energy. Clearly, $[(Nb_6Cl_{12})Cl_6]^{2-}$ is the extant species in solution when the RGC-OTE is held at 0.60 V.

Another interesting feature of the voltammograms of $[(Nb_6Cl_{12})Cl_6]^{4-}$ shown in Figure 1 is the reduction wave appearing at E_p = −1.30 V. This reduction wave exhibits an associated oxidation wave after the scan is reversed. The former is approximately the same size as the one-electron oxidation wave appearing at 0.01 V, suggesting that it too arises from a one-electron process. A similar reduction wave was observed by Klendworth and Walton[15a] for dichloromethane solutions containing the $[(Nb_6Cl_{12})Cl_2(PR_3)_4]$ complexes, and it was attributed to the quasireversible, one-electron reduction of the {Nb$_6$Cl$_{12}$}$^{2+}$ core unit to {Nb$_6$Cl$_{12}$}$^+$ as depicted in eq 1. The reduction wave at −1.30 V and associated oxidation wave were examined as a function of scan rate. It was found that $i_p/v^{1/2}$, E_p, and ΔE_p were independent of scan rate, although the latter was about 0.015 V
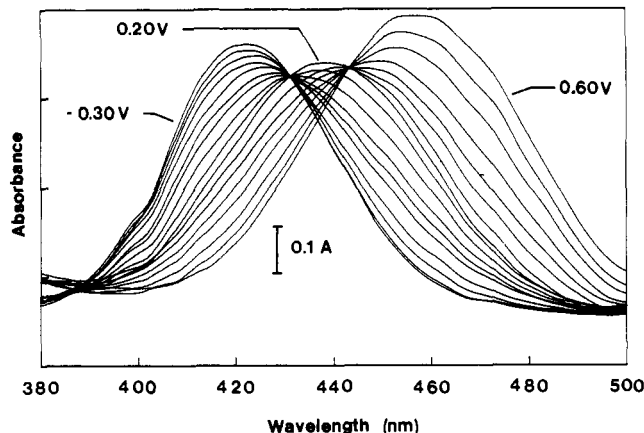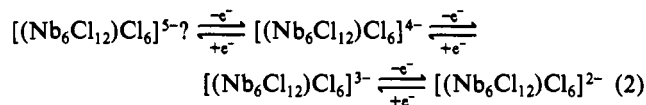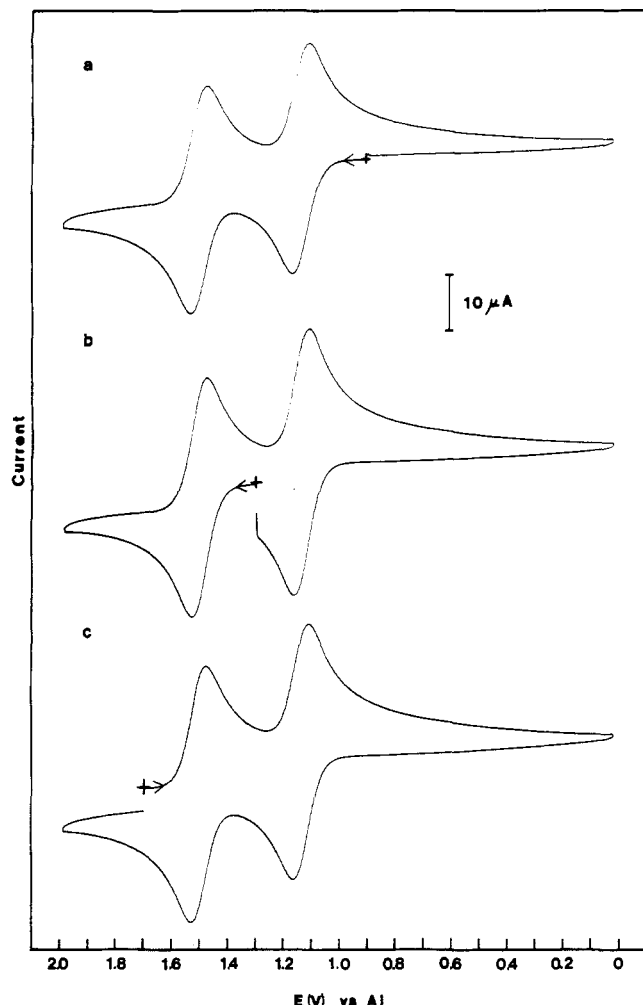
larger than expected for a one-electron reversible process at 100 °C. However, the peak current ratio for this pair of waves decreases slightly below 1 at slow scan rates, suggesting that the reduction product, most likely $[(Nb_6Cl_{12})Cl_6]^{5-}$, is only moderately stable on the time scale of the experiment. A controlled-potential electrolysis experiment that was conducted at an applied potential of −1.50 V at 100 °C with a solution of $[(Nb_6Cl_{12})Cl_6]^{4-}$ confirmed this result. The charge passed during this experiment was in considerable excess of that needed to effect the one-electron reduction of this cluster, and a brown intractable precipitate formed in the cell as the experiment progressed. A cyclic voltammogram of this solution recorded after several equivalents of charge had been passed indicated that virtually all of the cluster had been destroyed. Therefore, we did not attempt any further study of this reduction process nor did we attempt to characterize the reduction product. The one-electron reduction product of the related phosphine complex $[(Nb_6Cl_{12})Cl_2(P-n-Pr_3)_4]$ was also found to be unstable even when the temperature of the dichloromethane solvent was lowered to 0 °C.[15a] Thus, it is quite apparent from our results, and from results obtained previously for the related phosphine complexes, that those species containing the {Nb$_6$Cl$_{12}$}$^+$ core cluster inhibit only transient stability.

The electrochemistry of the hexameric niobium chloride clusters in basic AlCl$_3$-MeEtimCl is summarized as follows:

$$[(Nb_6Cl_{12})Cl_6]^{5-}? \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(Nb_6Cl_{12})Cl_6]^{4-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}$$

$$[(Nb_6Cl_{12})Cl_6]^{3-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(Nb_6Cl_{12})Cl_6]^{2-} \quad (2)$$

Acidic Melts. A representative cyclic voltammogram of a solution of $[MeEtim]_3[(Nb_6Cl_{12})Cl_6]$ prepared with the 60.0/40.0 mol % AlCl$_3$-MeEtimCl melt at room temperature and then exhaustively reduced at 0.90 V is shown in Figure 4. This voltammogram encompasses the nominal electrochemical window of acidic melt and was initiated from the rest potential; it bears certain qualitative similarities to those shown in Figure 1 for the {Nb$_6$Cl$_{12}$}$^{2+}$ core cluster in basic melt in that two successive oxidation waves with reverse currents are evident. However, the $E_{1/2}$ values for these two pairs of waves are shifted positively by more than 1 V relative to those in basic melt, and the reduction wave at E_p = −1.30 V in Figure 1 is not accessible within the potential window of acidic melt. Both E_p and $i_p/v^{1/2}$ for the oxidation wave at 1.17 V were independent of scan rate. The peak potential separation, ΔE_p, for this wave and its associated oxidation wave averaged 0.064 V over the range of scan rates from 0.010 to 0.200 V s^{-1}. This ΔE_p 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 average peak current ratio for this pair of waves was very close to 1.0 over this entire range of scan rates.

Figure 3. Absorption spectra of a 0.573 mM solution of (Nb$_6$Cl$_{12}$)-Cl$_2$·8H$_2$O in the 44.4/55.6 mol % AlCl$_3$-MeEtimCl melt at a reticulated glassy carbon optically transparent electrode as the potential is stepped sequentially from −0.30 V to +0.60 V. The temperature was approximately 25 °C.

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(27) See footnote 21 of ref 8 for a discussion of shifts in $E_{1/2}$ with pCl.

Figure 4. Cyclic voltammograms of niobium chloride clusters at a glassy carbon electrode in the 60.0/40.0 mol % AlCl₃–MeEtimCl melt at 40 °C: (a) 10.2 mM solution of [MeEtim]₃[(Nb₆Cl₁₂)Cl₆] after reduction at 0.90 V; (b) solution in (a) after oxidation at 1.30 V; (c) solution in (b) after oxidation at 1.70 V. The scan rates were 50 mV s⁻¹.
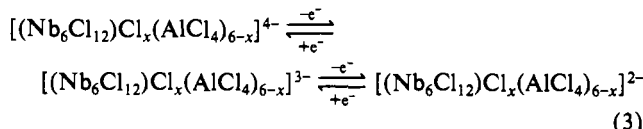
RDE voltammetric waves were recorded in a similar fashion by scanning the potential from the rest value toward more positive values. The resulting waves were typical of a mass-transport-controlled electrode process; plots of i_l versus $\omega^{1/2}$, constructed with data taken on the descending portion of the oxidation wave, were linear over the range of angular velocities extending from 105 to 209 rad s⁻¹, and they passed through the origin of each plot. In addition, plots of $\log [(i_l - i)/i]$ versus E were linear and gave slopes consistent with a value of $n = 1.0$. Thus, the oxidation of the extant species in acidic melt containing the {Nb₆Cl₁₂}²⁺ core unit is a one-electron, reversible process that is unaffected by coupled homogeneous chemistry on the voltammetric time scale.

Controlled-potential electrolysis experiments were conducted at 1.30 V in order to determine if stable bulk solutions of the oxidation product, which is expected to contain the original {Nb₆Cl₁₂}³⁺ core, could be prepared. A cyclic voltammogram of an exhaustively oxidized solution is shown in Figure 4b, and it exhibits the same waves shown in Figure 4a; i.e., no new species were produced other than the intended oxidation product. The solution color changed from light yellow to medium yellow-brown as the electrolysis experiment progressed. The voltammetric and spectral properties of this solution were identical to those of the original solution prepared with [MeEtim]₃[(Nb₆Cl₁₂)Cl₆] before reduction at 0.90 V, indicating that a species containing the {Nb₆Cl₁₂}³⁺ core unit was indeed produced during the electrolysis. As further evidence of this outcome, it was found that $E_{1/2}$ for the reduction of the electrolysis product was virtually the same as $E_{1/2}$ found during the oxidation of the species containing the {Nb₆Cl₁₂}²⁺ core (Table II).
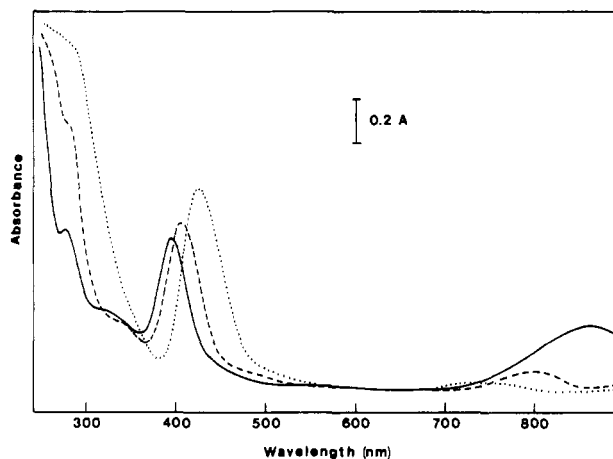
Figure 5. Absorption spectra of niobium chloride clusters in the 60.0/40.0 mol % AlCl₃–MeEtimCl melt at room temperature: (—) 1.11 mM solution of [MeEtim]₃[(Nb₆Cl₁₂)Cl₆] after reduction at 0.90 V; (---) foregoing solution after oxidation at 1.30 V; (⋯) same solution after oxidation at 1.70 V. The cell path lengths were 1.00 mm.

The second oxidation wave appearing at $E_p = 1.54$ V in Figure 4a, i.e., the wave corresponding to the oxidation of the species derived from the {Nb₆Cl₁₂}³⁺ core, was also examined with cyclic voltammetry. The voltammetric characteristics of this wave suggested that it also originated from a one-electron reversible electrode process. Therefore, controlled-potential electrolytic oxidation of a solution of the cluster based on the {Nb₆Cl₁₂}³⁺ core was undertaken at an applied potential of 1.70 V in order to determine if the oxidation product of this species was stable as well. The color of the solution changed from medium brown to dark brown during the course of the experiment. A cyclic voltammogram of the resulting solution is shown in Figure 4c, and it is obvious that no unexplained products were produced. The electrochemical and spectroscopic properties of the resulting solution were identical to those of a solution prepared by dissolving [MeEtim]₂[(Nb₆Cl₁₂)Cl₆] in this melt. Unlike the case for solutions prepared with basic melt (vide supra), no spontaneous reduction of the {Nb₆Cl₁₂}⁴⁺ core was observed, and these solutions were found to be stable indefinitely, provided that they were protected from the atmosphere. Taken together with the recent EXAFS[28a] and mass spectral[28b] data for cobalt(II) and nickel(II) coordination by [AlCl₄]⁻ in acidic melt, the foregoing results suggest the following redox scheme for niobium clusters in acidic melt:

$$[(Nb_6Cl_{12})Cl_x(AlCl_4)_{6-x}]^{4-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}$$

$$[(Nb_6Cl_{12})Cl_x(AlCl_4)_{6-x}]^{3-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(Nb_6Cl_{12})Cl_x(AlCl_4)_{6-x}]^{2-}$$

$$(3)$$

Electrochemical data for these reactions are summarized in Table II.

Absorption spectra of clusters in acidic melt derived from the {Nb₆Cl₁₂}ᶻ⁺ ($z = 2–4$) core units are depicted in Figure 5. Absorption maxima and absorptivities taken from these spectra are collected in Table I. The oxidation level of the cluster in each solution was adjusted by using controlled-potential electrolysis exactly as described above, except that these solutions were much more dilute than those used for voltammetry. Qualitatively, these spectra are somewhat similar to those recorded for the anionic chloride complexes containing the {Nb₆Cl₁₂}ᶻ⁺ core in basic melt, confirming the conclusion reached from the electrochemical results that solutes derived from these hexameric cores are also present in acidic melt. However, the acidic spectra are shifted to shorter wavelengths relative to the spectra recorded in basic melts, and

(28) (a) Dent, A. J.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Chem. Commun.* **1990**, 315. (b) Abdul-Sada, A. K.; Seddon, K. R.; Welton, T. *Org. Mass Spectrom.*, submitted for publication.

therefore, in eq 3, x cannot be 6.

From these electrochemical and spectroscopic results, it is obvious that electroactive species derived from the {Nb$_6$Cl$_{12}$}$^{z+}$ core unit are stable in the very Lewis acidic environment of the 60.0/40.0 mol % melt. However, because the $E_{1/2}$ values for the {Nb$_6$Cl$_{12}$}$^{2+/3+}$ and {Nb$_6$Cl$_{12}$}$^{3+/4+}$ reactions are shifted positively from their values in basic melt by more than 1 V, it is very unlikely that the extant cluster species in acidic melt are coordinated by the full complement of 18 chlorides. It is sometimes possible to determine the number of chloride ions lost during the dissolution of a chloride-containing complex or compound in the so-called "neutral–acidic" melt[29] by monitoring the decrease in the voltammetric current for the reduction of [Al$_2$Cl$_7$]$^-$.[30] Several such experiments were attempted by adding small amounts of [MeEtim]$_3$[(Nb$_6$Cl$_{12}$)Cl$_6$] to such a melt at 100 °C. As expected, a decrease in the [Al$_2$Cl$_7$]$^-$ concentration consistent with the loss of chloride ion from the anionic cluster was found upon the dissolution of this salt. However, despite considerable effort on our part, it was not possible to obtain any really useful quantitative information from these experiments due to the very limited solubility of the cluster and to the poor reproducibility of the [Al$_2$Cl$_7$]$^-$ voltammetric reduction wave at glassy carbon at 100 °C. Although the value of x in eq 3 could not be established, the available evidence suggests that it is less than 6 and could in fact be zero. Structural and spectroscopic considerations require that the 12 bridging chlorides be retained in the core cluster.

Diffusion Coefficients. Diffusion coefficients, D, and Stokes–Einstein products, $D\eta/T$, where η is the absolute viscosity of the melt and T is the absolute temperature, are collected in Table II. $D\eta/T$ is inversely proportional to the solvodynamic radius, r_{solv}, of the diffusing species through the Stokes–Einstein equation:

$$D\eta/T = k/C\pi r_{\text{solv}} \qquad (4)$$

In this equation, k is the Boltzmann constant and C is a numerical constant that is often assigned a value of 6. The diffusion coefficients and Stokes–Einstein products in this table are the composite values resulting from numerous linear-sweep and RDE voltammetry experiments. Several conclusions can be drawn from the results in Table II. First, r_{solv} of the various niobium clusters in acidic and basic melts are independent of the oxidation level of the cluster within the precision of the experimental measurements. This stands in contrast to what has been observed previously for simple monomeric and dimeric complexes.[31] Second, the cluster radii in basic melt appear to be only about 70% of those

found in acidic melt. Finally, from these data it appears that the average r_{solv} of the anionic niobium clusters is somewhat larger than that of a structurally similar hexameric anionic transition metal cluster that was previously examined in this melt, [(Mo$_6$Cl$_8$)Cl$_6$]$^{2-}$ ($D\eta/T$ = 1.6 × 10^{-10} g cm s^{-2} K^{-1}).[7] This latter result is expected because the anionic niobium clusters are physically larger; i.e., they are coordinated to a greater number of chlorides and the M–M bond distance in the niobium species is longer, ~2.90 Å versus ~2.60 Å.[12] The difference in radius between the acidic and basic clusters is in accord with the formulation of the acidic species as depicted in eq 3, probably with x = 0. Such coordination is predicted to lead to a significant reduction in radius on going from [(Nb$_6$Cl$_{12}$)(AlCl$_4$)$_6$]$^{2-}$ to [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{2-}$ as judged from an MM2 molecular mechanics simulation.[22] It is hoped that a better understanding of the factors leading to these results will be obtained as related hexameric clusters such as [(W$_6$Cl$_8$)Cl$_6$]$^{2-}$ and [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{(6-z)-}$ (z = 2–4) are investigated.

Summary

Anionic chloride complexes of the {Nb$_6$Cl$_{12}$}$^{z+}$ (z = 1–4) core clusters with the general formula [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{(6-z)-}$ were found in basic melt, but the cluster species corresponding to z = 1 and 4 exhibited only limited stability. The former appears to be inherently unstable, as was reported for the related phosphine complexes, whereas the latter appears to be reduced to the z = 3 cluster by chloride ion in basic melt. Species containing the z = 2–4 core clusters were stable in acidic melt. The {Nb$_6$Cl$_{12}$}$^{2+/3+}$ and {Nb$_6$Cl$_{12}$}$^{3+/4+}$ electrode reactions were found to be mass-transport-controlled in both acidic and basic melts, in contrast to the quasireversible behavior or mixed control reported for the related phosphine clusters in dichloromethane. It was not possible to determine the exact chloride coordination of these niobium cluster species in acidic melts; however, the large positive potential shifts observed for the above electrode reactions on passing from basic melt to acidic melt suggests that some of the labile chloride ions associated with the [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{(6-z)-}$ complexes have been replaced by [AlCl$_4$]$^-$ ions to give species of the type [(Nb$_6$Cl$_{12}$)Cl$_x$(AlCl$_4$)$_{6-x}$]$^{(6-z)-}$ (x = 1–6).

Registry No. [MeEtim]$_3$[(Nb$_6$Cl$_{12}$)Cl$_6$], 139460-77-8; [MeEtim]$_2$-[(Nb$_6$Cl$_{12}$)Cl$_6$], 139460-78-9; [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{4-}$, 12515-95-6; [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{3-}$, 12515-94-5; [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{2-}$, 12515-93-4; [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{5-}$, 131005-54-4; AlCl$_3$, 7446-70-0; MeEtimCl, 65039-09-0; C, 7440-44-0; (Nb$_6$Cl$_{12}$)Cl$_2$, 138007-73-5.

(29) "Neutral–acidic" melt is 50.0/50.0 mol % melt, i.e., [MeEtim]$^+$[AlCl$_4$]$^-$ containing a slight excess of AlCl$_3$. This excess AlCl$_3$ reacts completely with the [AlCl$_4$]$^-$ to produce a small quantity of [Al$_2$Cl$_7$]$^-$.

(30) Lipsztajn, M.; Osteryoung, R. A. *Inorg. Chem.* **1985**, *24*, 716.

(31) Hussey, C. L.; Sun, I-W.; Strubinger, S. K. D.; Barnard, P. A. *J. Electrochem. Soc.* **1990**, *137*, 2515.