constants C_N and $C_{N'}$ of the ethylenic protons and of the acetate protons in these cyclic structures change with pH in a different way depending on the type of proton considered.[6,7] This results from changes in conformational equilibria of the various groups caused by restricted flexibility, electrostatic repulsions and hydrogen bond formation that are difficult to predict a priori. These restrictions seem to be even more severe in the cyclic triaza macrocycles than in the tetraaza analogues.

The constants log K_1 and log K_2 refer to equal statistical protonation of the nitrogen atoms in the ring. The constant log K_3 = 2.88 is similar to log K_3 for EDTA and remarkably lower than the values log K_3 and log K_4 reported for DOTA, which reflect the protonation of the two carboxylate moieties not adjacent to a protonated nitrogen atoms in the H_2L^{2+} form of DOTA. The log K_3 value in NOTA, which refers to protonation of the first carboxylate group in the H_2L^{2+} form, is lower because each carboxylate group is 66% hydrogen bonded to an adjacent nitrogen atom which bears 66% of a positive charge. The last three protonation constants, which reflect protonation of the remaining two carboxylates and a single ring nitrogen, are even lower for two reasons. The two carboxylate groups are now fully hydrogen bonded to their adjacent positively charged nitrogens while protonation of the last nitrogen is constrained by the electrostatic repulsions imposed by a nine-membered ring containing three positively charged nitrogens.

There are conformational similarities between the lanthanide complexes of the polyaza macrocycles, NOTA and DOTA, and the hydrocarbon analogues of these cycles. It has been shown[13] that the tetraaza cycle of DOTA, like the 12-membered ring of cyclododecane,[31,34] has two favored enantiomeric square [3333] conformations, whereas both the triaza cycle of NOTA and the 9-membered ring of cyclononane have two favored enantiomeric triangular [333] conformations (each enantiomer has four or three identical ethylenic groups with conformations δ or λ). Previous dynamic NMR measurements[32,39] have shown that the energy barrier for interconversion between these ring conformations is smaller in cyclononane (25 kJ mol^{-1}) than in cyclododecane (30.5 kJ mol^{-1}). This same trend is preserved in the lanthanide complexes of NOTA vs. those of DOTA. The NMR data reported in this work for La(NOTA) and Lu(NOTA) shows that the 9-membered ring in these complexes is much more flexible than the 12-membered ring in the corresponding DOTA complexes.[13] Although the barrier for ethylene ring conformational changes is similar in La(DOTA) (60.7 kJ mol^{-1})[13] and the hydroxo complex of Lu(NOTA) (~64 kJ mol^{-1}), the smaller triaza macrocycle requires the smaller lanthanide cation, Lu^{3+}, for structural rigidity. Also a correlation is found between the conformational rigidity of these complexes and their kinetics of formation; i.e., the NOTA complexes are flexible and somewhat more labile while the DOTA complexes are rigid and quite inert. Therefore, the conformational characteristics of the cyclic ring in these chelated ligands are, in part, determined by the extent of encapsulation of a lanthanide cation in addition to its own steric requirements.

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Registry No. 1, 56491-86-2; **3**, 96556-05-7; La(NOTA), 78085-47-9; Lu(NOTA), 98331-80-7.

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Raman Spectroscopic Investigation of Alkali-Metal Hexachloro Compounds of Refractory Metals

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The Raman spectra of molten alkali-metal hexachlorozirconate, hexachlorohafnate, hexachloroniobate, and hexachlorotantalate compounds have been obtained in the temperature range 623–1143 K. The results confirm that the refractory metal exists in the form of an octahedrally coordinated complex anion that is stable even in the molten state. For a given refractory metal the frequency of the ν_1 line increases as the size of the alkali-metal cation decreases. For a given alkali metal the frequency of the ν_1 line increases as the valence of the refractory metal increases. This last observation may serve as the basis for detecting, by Raman spectrocopy, aliovalent species that may form during the electrolysis of melts containing refractory-metal chlorides.

Introduction

The chlorides of the elements of groups 4 and 5[22] react with alkali-metal chlorides to produce hexachloro compounds of the general formulas A_2MCl_6 and $ANCl_6$, where A is an alkali metal, M is a group 4 metal, and N is a group 5 metal. The volatile covalently bonded refractory-metal chlorides exist in thermodynamically stable forms in these compounds, which, when dissolved in alkali-metal chloride melts, constitute potential electrolytes for the electrodeposition of the refractory metals. However, their electrolytic recovery is impaired by the formation of aliovalent species, which are difficult to identify during electrolysis.

In order to determine whether Raman spectroscopy can be useful in this regard, the Raman spectra of melts of the following compounds were measured: Na_2ZrCl_6, K_2ZrCl_6, Cs_2ZrCl_6, Li_2HfCl_6, Na_2HfCl_6, K_2HfCl_6, Cs_2HfCl_6, $KNbCl_6$, $CsNbCl_6$, $NaTaCl_6$, $KTaCl_6$, $CsTaCl_6$.

Experimental Section

The zirconium and hafnium hexachloro compounds were synthesized in this laboratory by the reaction of $ZrCl_4$ or $HfCl_4$ vapor with solid alkali-metal chloride under controlled pressure and temperature conditions. The preparation has been described elsewhere.[2-5] The niobium

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Table I. Raman Spectral Data for Molten Alkali-Metal Hexachlorozirconates and Hexachlorohafnates

			Raman, cm^{-1}	
compd	compn $X_{A_2MCl_6}$	temp, K	this work	previous work
Na_2ZrCl_6	0.814	933	330 s, p[a] 145 s	
K_2ZrCl_6	1.000	1123	325 s, p 148 s	
Cs_2ZrCl_6	1.000	1123	323 s, p 153 s	326 s; ν_1 (A_{1g})[b,c] 249 w; ν_2 (E_g) 161 s; ν_5 (T_{2g})
Li_2HfCl_6	0.387	813	338 s, p 153 s	
Na_2HfCl_6	0.724	958	338 s, p 156 s	
K_2HfCl_6	1.000	1123	323 s, p 153 s	
Cs_2HfCl_6	1.000	1143	329 s, p 156 s	333 s; ν_1 (A_{1g})[b,c] 261 w; ν_2 (E_g) 167 s; ν_5 (T_{2g})

[a] Abbreviations: s = strong; m = medium; w = weak; p = polarized. [b] Reference 14, solid specimens, $T = 298$ K. [c] O_h point group symmetry.

and tantalum hexachloro compounds were synthesized by the same technique using $NbCl_5$ and $TaCl_5$ vapors, respectively.[6] In addition, $CsNbCl_6$ and $CsTaCl_6$ were synthesized by precipitation from solutions of $SOCl_2$–ICl.[7,8] The hexachloro compounds have been characterized by X-ray powder diffraction;[5,6] in addition, their vapor pressures have been measured.[3-5,9]

In an argon-filled glovebox the samples were loaded into optical cells that were constructed from square fused-quartz tubing, 1 cm on edge. The cells were evacuated and flame-sealed. Specimens were heated by a method somewhat different from those previously employed in spectroscopic studies. This was due to the need to accommodate the larger laboratory-scale light-metal electrolysis cells for in situ Raman scattering studies also in progress.[10,11] Specifically, an electrical resistance tube furnace was designed and built. It consisted of nichrome wire wrapped around a vertical fused-quartz tube, 2.5 cm in diameter × 30 cm long, which was contained in a can packed with aluminosilicate insulating fiber. To permit irradiation and observation of the sample in the furnace, three side-arm tubes, which served as windows, were connected to the vertical tube. Located in the same horizontal plane and in a tee configuration, the side arms were heated by independently controlled nichrome windings to maintain a constant temperature in the sample. The maximum operating temperature of this furnace was 1273 K.

The Raman instrumentation consisted of the following. Exciting radiation was provided by either an Ar^+ laser, Coherent Innova Model 90-4, or a Kr^+ laser, Coherent Innova Model 90-K. The spectrometer was a triple monochromator, Spex Industries, Triplemate, fitted with an intensified silicon photodiode array, EG&G PARC Model 1420-3. The data were recorded on an optical multichannel analyzer, EG&G PARC Model OMA2.

The spectra of the hexachlorozirconates and hexachlorohafnates, which are transparent as melts, were obtained by using the 514.5-nm line of Ar^+ at a typical power of 1.3 W. The spectra of the hexachloroniobates and hexachlorotantalates, which are deeply colored as melts, were obtained by using the 647.1-nm line of Kr^+ at a typical power of 600 mW. The exception was $KTaCl_6$, for which better spectra were obtained with the argon line.

The plane of polarization of the exciting radiation is set by a polarization rotator (${}^{\perp}I$ or ${}^{\parallel}I$). The beam then passes horizontally through the molten sample. The scattered radiation is collected at 90° and is imaged onto the vertical entrance slit of the spectrometer while passing through a vertical polarization analyzer ($I_{\perp}$ always). The spectrometer slit width is 100 μm, which is equivalent to $\sim$6 cm^{-1}. The spectra were recorded for approximately 1 min, corresponding to 200 scans on the OMA, which was calibrated by using the emission lines of a neon lamp in the green and krypton plasma lines in the red.[12]

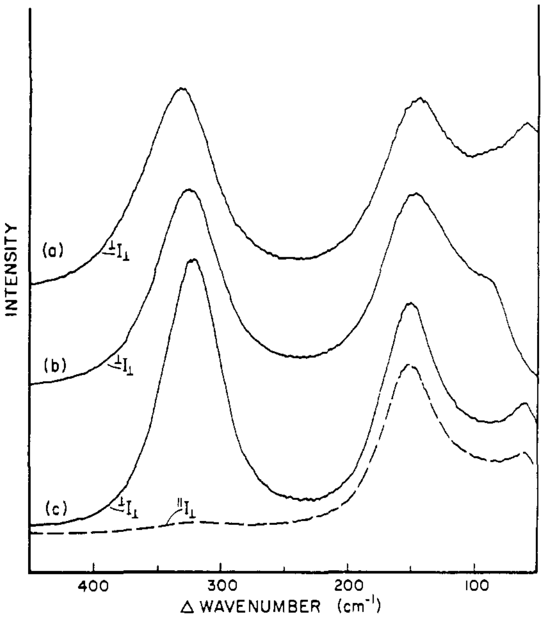

Figure 1. Raman spectra of molten alkali-metal hexachlorozirconates (514.5-nm excitation): (a) Na_2ZrCl_6 at 933 K; (b) K_2ZrCl_6 at 1123 K; (c) Cs_2ZrCl_6 at 1123 K.

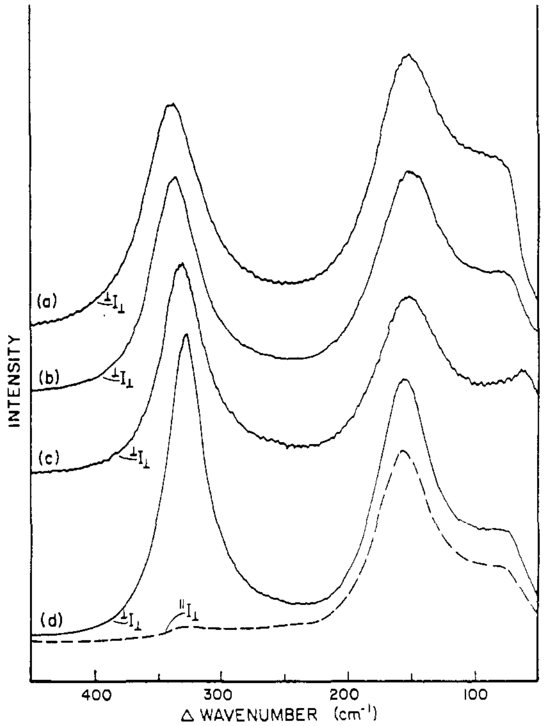

Figure 2. Raman spectra of molten alkali-metal hexachlorohafnates (514.5-nm excitation): (a) Li_2HfCl_6 at 813 K; (b) Na_2HfCl_6 at 958 K; (c) K_2HfCl_6 at 1123 K; (d) Cs_2HfCl_6 at 1143 K.

The spectra were taken at temperatures approximately 30 K above the liquidus or at the decomposition temperature, i.e. the temperature at which the sample pressure is 1 atm, whichever is lower.

Results and Discussion

1. Alkali-Metal Hexachlorozirconates and Hexachlorohafnates. The characteristics of the Raman spectra of the molten alkali-metal hexachlorozirconates and hexachlorohafnates are given in Table I. Because Na_2ZrCl_6, Li_2HfCl_6, and Na_2HfCl_6 decompose

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Table II. Raman Spectral Data for Molten Alkali-Metal Hexachloroniobates and Hexachlorotantalates

			Raman, cm^{-1}		
				previous work	
compd	compn X_{ANCl_6}	temp, K	this work	solid, 298 K	melt
$KNbCl_6$	0.808	723	370 s, p[a] 170 m		
$CsNbCl_6$	1.000	823	366 s, p 178 m	369 s (A_{1g})[b] 289 w (E_g) 183 s 175 s } (T_{2g})	373 p (A_{1g})[d] 281 (E_g) 181 173 } (T_{2g})
$NaTaCl_6$	0.901	623	389 s, p 172 m		
$KTaCl_6$	0.993	723	387 s, p 182 m	386 vs[c] 302 vw, br 187 m 184 m	390 s, p[c] 183 m
$CsTaCl_6$	1.000	873	379 s, p 179 m	382 s (A_{1g})[b] 299 w (E_g) 188 180 } (T_{2g})	

[a] Abbreviations: s = strong; m = medium; w = weak; br = broad; p = polarized. [b] Reference 14, assuming free ion, O_h point group symmetry. [c] Reference 15, $T = 693$ K. [d] Reference 17, $T = 873$ K.

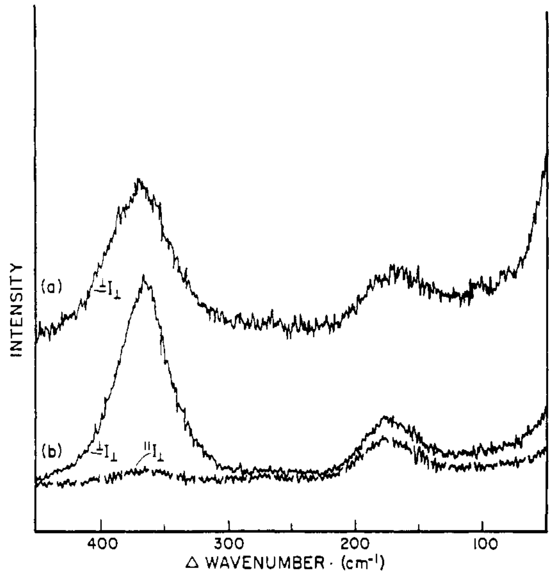

Figure 3. Raman spectra of molten alkali-metal hexachloroniobates (647.1-nm excitation): (a) $KNbCl_6$ at 723 K; (b) $CsNbCl_6$ at 823 K.

below their melting points, samples of these compounds were diluted with the corresponding alkali-metal chloride in order to produce a stable melt.[4,13] The spectra of the hexachlorozirconates and hexachlorohafnates are shown in Figures 1 and 2, respectively. For the sake of brevity the spectra are shown only over the range 50–450 cm^{-1}, although the data were recorded out to 700 cm^{-1}. Furthermore, in each figure, the spectra for both polarization orientations are given only for the cesium compound. While the intensity is in arbitrary units, the same scale factor has been used on all spectral traces. The "peaks" around 60 cm^{-1} are due to the monochromator filter cutoff.

There are no reports in the literature of Raman spectra of these melts. Spectra for Cs_2ZrCl_6 and Cs_2HfCl_6 have been measured in the solid state at room temperature.[14] These spectra were interpreted as evidence for a free octahedrally coordinated MCl_6^{2-} ion, O_h point group symmetry. While the melt spectra suffer from broadening of the strong peaks and absence of the weak peaks, there is sufficient similarity in solid and liquid spectra to suggest that MCl_6^{2-} is present and stable in these melts.

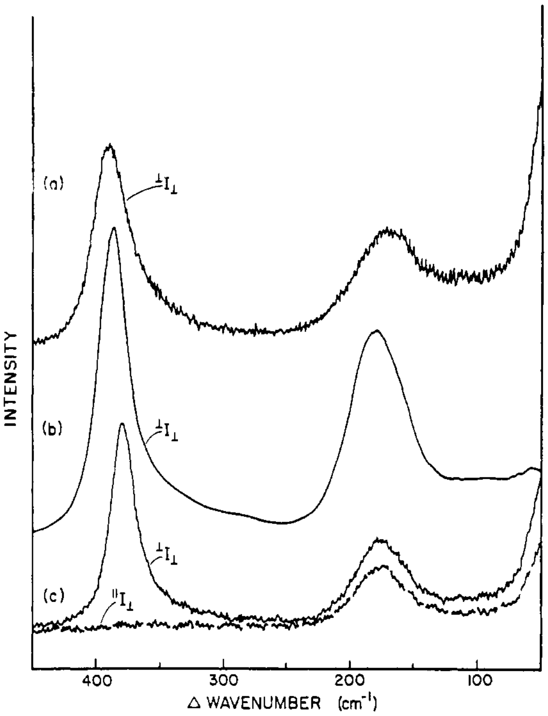

Figure 4. Raman spectra of molten alkali-metal hexachlorotantalates: (a) $NaTaCl_6$ at 623 K; (647.1-nm excitation); (b) $KTaCl_6$ at 723 K (514.5-nm excitation); (c) $CsTaCl_6$ at 873 K (647.1-nm excitation).

In Table I there appears to be a small shift in the position of the ν_1 peak with a change in alkali-metal cation, where ν_1 decreases as the size of the cation increases. Such a trend has also been observed in alkali-metal chlorotitanate systems.[16] Table I also shows that for a given alkali metal, the ν_1 peaks are virtually identical for the zirconium and hafnium compounds. This demonstrates the strong chemical similarity between these two elements as explained by the lanthanide contraction.

The commonest impurity in such melts is the oxychloride, which may be soluble or insoluble. If insoluble, it appears as black particles floating on the surface and therefore does not adversely affect the melt spectra. If soluble, the oxychloride should be detectable by the appearance of a band near 900 cm^{-1} [14]. The latter was not observed in any of the spectra reported in this work.

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2. Alkali-Metal Hexachloroniobates and Hexachlorotantalates. The Raman spectra of the molten alkali-metal hexachloroniobates and hexachlorotantalates are shown in Figures 3 and 4, respectively. The scale factors within this set are identical except for those of the KTaCl$_6$ spectra. The characteristics of these spectra are given in Table II, which also includes results from the literature.

Mamantov et al.[15] have measured the Raman spectra of KTaCl$_6$ at 693 K. The results obtained in this work are in excellent agreement given the small differences in specimen composition and temperature in the two studies. For CsNbCl$_6$ there is good agreement between the results obtained in this work and those of Øye et al.[17] However, in this work it was not possible to detect the weak band in the vicinity of 280 cm^{-1} or to resolve the peak at 178 cm^{-1} into the reported components.[17]

As for Cs$_2$ZrCl$_6$ and Cs$_2$HfCl$_6$ mentioned above, the existence of the octahedrally coordinated NCl$_6^-$ ion has been proposed on the basis of spectral measurements of solid CsNbCl$_6$,[17] KTaCl$_6$[15] and CsTaCl$_6$.[14]

As was the case in Table I, in Table II there appears to be a small shift in the position of the ν_1 peak with a change in alkali-metal cation, where ν_1 decreases as the size of the cation increases. In contrast to Table I, Table II shows that for a given alkali metal, there is a shift in the position of the ν_1 peak with a change in refractory metal, where ν_1 increases with atomic number. This demonstrates that the similarity in the chemical behaviors of niobium and tantalum is not as pronounced as is the case for zirconium and hafnium.

3. General Observations. The refractory-metal compounds studied in this work exhibited behavior in conformity with the existence of octahedrally coordinated species of the O_h point group symmetry, although the constituent refractory-metal chlorides possess different symmetries. In fact, group 4 chlorides are of a symmetry different from that of the group 5 chlorides. ZrCl$_4$ and HfCl$_4$ have T_d symmetry, while NbCl$_5$ and TaCl$_5$ have D_{3h} symmetry.[19-21]

Comparison of Tables I and II reveals that it may be possible on the basis of the Raman spectrum to detect changes in valency of refractory-metal species in these melts. Specifically, the ν_1 peaks of K$_2$ZrCl$_6$ and K$_2$HfCl$_6$ lie at ~325 cm^{-1} while the corresponding peaks of KNbCl$_6$ and KTaCl$_6$ lie at 370–390 cm^{-1}. This represents a shift of approximately 55 cm^{-1} in changing from the analogous group 4 to group 5 compounds. In an investigation of chlorotitanates, a shift of 30 cm^{-1} was noted on going from Ti^{4+} to Ti^{3+}.[17] Because these shifts are easily detectable in the Raman spectra of these melts, it should be possible to conduct spectroreducibility studies.

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Registry No. Na$_2$ZrCl$_6$, 18346-98-0; K$_2$ZrCl$_6$, 18346-99-1; Cs$_2$ZrCl$_6$, 16918-86-8; Li$_2$HfCl$_6$, 18346-97-9; Na$_2$HfCl$_6$, 12016-11-4; K$_2$HfCl$_6$, 19381-63-6; Cs$_2$HfCl$_6$, 16918-87-9; KNbCl$_6$, 16919-88-3; CsNbCl$_6$, 16921-14-5; NaTaCl$_6$, 16920-14-2; KTaCl$_6$, 16918-73-3; CsTaCl$_6$, 16921-15-6.

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Desolvation Energies for Rare-Earth-Metal Perchlorate, Chloride, and Nitrate Electrolytes from 0.1 *m* to Saturation

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Work of desolvation values for rare-earth-metal perchlorate, chloride, and nitrate electrolytes across the rare-earth-metal series from 0.1 to 1 *m* are relatively uniform and are in the sequence of perchlorates > chlorides > nitrates. Changes in $T\Delta S$ in this region are in the sequence of perchlorates > nitrates > chlorides and reveal a geometric anion obstruction factor that depends on anion size and complexity. Desolvation energies for 0.2 *m* increments for the region of 1 *m* to saturation show that negative values of $T\Delta S$ persist to saturation for the perchlorate series but $T\Delta S$ values for chlorides all change from negative to positive near saturation. For the nitrate series at saturation, incremental values of $T\Delta S$ are negative for lanthanum through gadolinium, near zero for terbium, dysprosium, holmium, and erbium, and positive for thulium, ytterbium, and lutetium. Zero crossing of incremental $T\Delta S$ is interpreted to be an indicator that outer-sphere ion pairing is complete, and positive $T\Delta S$ is the result of ion compression of inner-sphere cation water and electrolyte destructuring on formation of inner-sphere ion pairs by water displacement.

Introduction

In a previous paper we used a desolvation method to calculate crystallization energies of rare-earth-metal perchlorates, chlorides, and nitrates.[1] Gibbs energy changes were calculated from solvent activity data of Spedding and co-workers,[2-4] Rard and Spedding,[5,6] and Rard, Miller, and Spedding.[7] Inverse heat of dilution data[8-11] were combined with ΔG values in the second law of thermody-

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