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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 ~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]

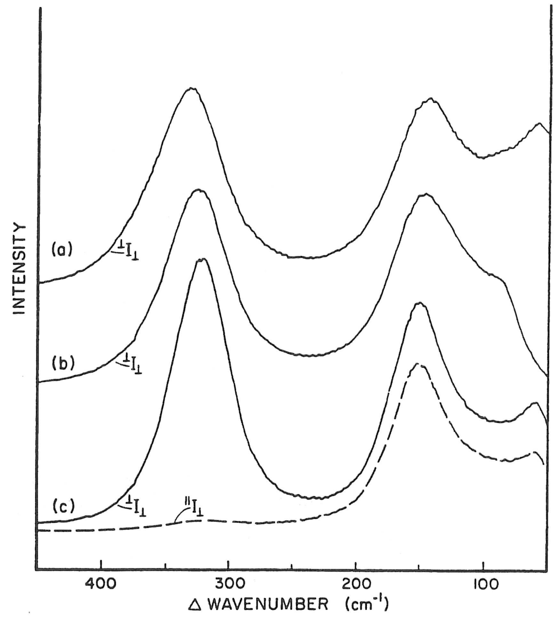

Figure 1. Raman spectra of molten alkali-metal hexachlorozirconates (514.5-nm excitation): (a) Na_2ZrCl_6 at 933 K; (b) K_2ZrCl_6 at 1123 K; (c) Cs_2ZrCl_6 at 1123 K.

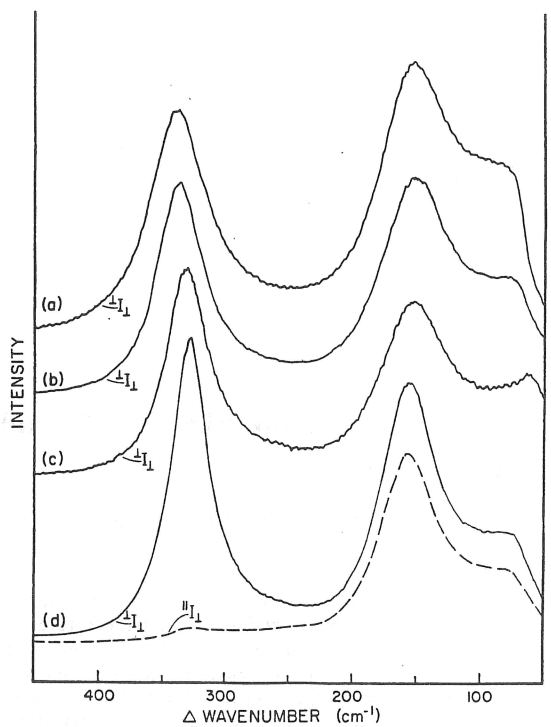

Figure 2. Raman spectra of molten alkali-metal hexachlorohafnates (514.5-nm excitation): (a) Li_2HfCl_6 at 813 K; (b) Na_2HfCl_6 at 958 K; (c) K_2HfCl_6 at 1123 K; (d) Cs_2HfCl_6 at 1143 K.

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

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

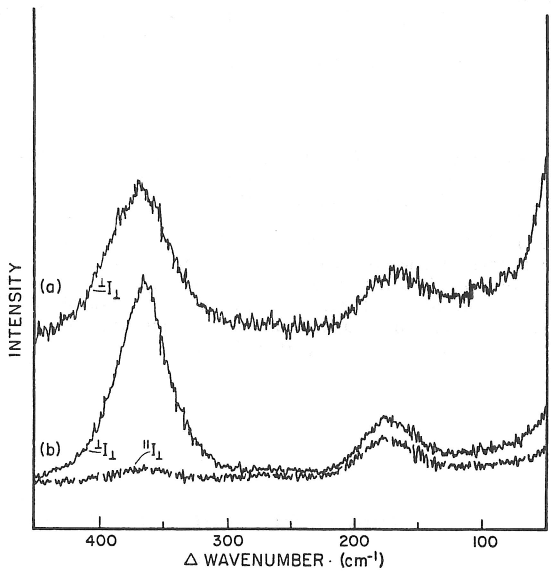

Figure 3. Raman spectra of molten alkali-metal hexachloroniobates (647.1-nm excitation): (a) $KNbCl_6$ at 723 K; (b) $CsNbCl_6$ at 823 K.

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.

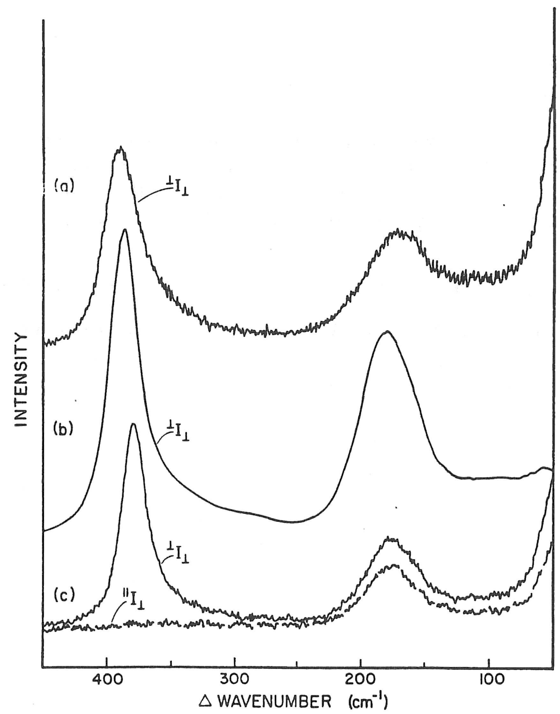

Figure 4. Raman spectra of molten alkali-metal hexachlorotantalates: (a) $NaTaCl_6$ at 623 K; (647.1-nm excitation); (b) $KTaCl_6$ at 723 K (514.5-nm excitation); (c) $CsTaCl_6$ at 873 K (647.1-nm excitation).

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_2ZrCl_6 and Cs_2HfCl_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_2ZrCl_6 and K_2HfCl_6 lie at $\sim$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_2ZrCl_6, 18346-98-0; K_2ZrCl_6, 18346-99-1; Cs_2ZrCl_6, 16918-86-8; Li_2HfCl_6, 18346-97-9; Na_2HfCl_6, 12016-11-4; K_2HfCl_6, 19381-63-6; Cs_2HfCl_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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(22) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)