CHANGES OF VIBRATIONAL MODES UPON MELTING
CsHgCl₃, Cs₂HgCl₄ AND Cs₃HgCl₅ SOLIDS AND
RAMAN SPECTRA OF HgCl₂-ACl (A=Li,Na,K,Cs)
MOLTEN SALT MIXTURES

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ABSTRACT
Spectra of polycrystalline CsHgCl₃, Cs₂HgCl₄ and Cs₃HgCl₅ have
been measured from LN₂ to temperatures above melting. The Raman
spectra for the Cs₃HgCl₅ solid are in agreement with the discrete
tetrahedral HgCl₄²⁻ species present in crystal structure. The spectral
changes occurring on melting Cs₂HgCl₄ and Cs₃HgCl₅ suggest the
retention of the HgCl₄²⁻ tetrahedral configurations. Upon melting
CsHgCl₃, the coordination of Hg in the crystal changes and melt
microstructure is better characterized by a planar HgCl₃ type complex
formation. The Raman spectra of molten HgCl₂-ACl (A=Li,Na,K,Cs)
mixtures have been also measured at different compositions and
temperatures up to 973 K. At high alkali halide concentration range, the
HgCl₄²⁻ and HgCl₃ configurations seem to be stabilized by the Cs⁺, K⁺
and Na⁺, Li⁺ ions respectively.

INTRODUCTION
The formation of complex ions in charge-unsymmetrical binary molten salt systems
MCl₂-ACl (M=Be,Mg,Mn,Fe,Ni & A=Li...Cs) has been extensively investigated by
spectroscopic (1) and thermodynamic (2) methods. The examination of the vibrational
spectra of MCl₂-ACl mixtures in the molten state has revealed that several spectral changes
occur which depend on composition and/or on substituting the alkali metal cation from Li
to Cs. For mixtures rich in AC₁ both spectroscopic and thermodynamic measurements
indicate that the MO₄³⁻ tetrahedra are the predominant "complex-ion" species. Raman
spectroscopy has been already used to identify and characterize solid compounds formed
in the binary system and to study the changes of vibrational frequencies upon
melting (1,3).

In the present work, Raman spectroscopy is used (a) for determining the changes of
vibrational modes occurring upon melting CsHgCl₃, Cs₂HgCl₄ and Cs₃HgCl₅ solids.
(b) for correlating the solid and liquid structures and (c) for characterizing the melt microstructure of the HgCl$_2$-ACl (A=Li,Na,K,Cs) molten salt mixtures.

EXPERIMENTAL

Mercury (II) chloride (Merck Chemical Co.) was purified by several sublimations in Pyrex tubes at a small temperature gradient around its melting point. CsCl (Cerac Pure Inc.) was repeatedly sublimed in high dynamic vacuum, while LiCl (Alpha) was cleaned by bubbling gaseous HCl through the melt and then filtering under N$_2$ atmosphere. NaCl and KCl (Merck Chemical Co.) were further purified by recrystallization. The anhydrous materials were handled in Pyrex tubes sealed in vacuum or in a N$_2$-atmosphere drybox with a water vapor content of less than 1 ppm.

Raman cells were made of fused-silica tubing: 3 mm i.d., 4 mm o.d. and 30 mm length. All cells were thoroughly cleaned, baked out to red-heat, and degassed by evacuation while hot. The total amount of chemicals added to the cells was approximately 180 mg. Samples of CsHgCl$_3$, Cs$_2$HgCl$_4$, Cs$_3$HgCl$_5$ and all HgCl$_2$-ACl mixtures were prepared by mixing and heating together the appropriate amounts of the corresponding starting materials.

Raman spectra were recorded on a Spex 1403 double monochromator equipped with high-temperature cell device as described elsewhere (4).

RESULTS AND DISCUSSION

CsHgCl$_3$: solid and melt

A number of crystal structures, some of which are polymorphic modifications, have been reported for the CsCl/HgCl$_2$ (1/1) compound (5,6). Zvonkova et al. have proposed (5) a deformed perovskite structure for CsHgCl$_3$ in which Hg has 2 Cl neighbors at 2.29 Å and 4 Cl at 2.70 Å, an eventually deformed octahedral configuration. In Fig. 1 the Raman spectra of polycrystalline CsHgCl$_3$ from LN$_2$ to the premelting temperature of 523 K are shown. A number of Raman peaks are clearly visible and the strong band situated at 231 cm$^{-1}$ (at 77 K) is attributed to Hg-Cl symmetrical stretching mode. The appearance of these bands excludes an ideal perovskite structure for CsHgCl$_3$ for which no Raman activity is expected.

The Hg-Cl stretching frequency of pure polycrystalline HgCl$_2$ has been reported (7) at ~319 cm$^{-1}$ (at 77 K) and is attributed to the presence of HgCl$_2$ molecules in the lattice. The remarkable red shift (of ~ 90 cm$^{-1}$) of the Hg-Cl stretching frequency observed on going from HgCl$_2$ to CsHgCl$_3$ certainly indicates an increase in the coordination number of Hg, accounting most probably for an octahedral configuration around Hg in the CsHgCl$_3$ crystal. Thus, the interpretation of the vibrational spectra of CsHgCl$_3$, in terms of a molecular or quasi-molecular HgCl$_2$ unit (8), seems to be incomplete. Furthermore with increasing temperature there is a slight blue shift of the Hg-Cl stretching frequency from...
231 at LN\textsubscript{2} to 245 cm\textsuperscript{-1} at 523 K and a corresponding half width broadening, which imply that no phase transitions exist in this temperature range.

The Raman spectra of molten CsHgCl\textsubscript{3} is shown on the top of Fig. 1 at 723 K. The main feature of the spectra is a strong polarized band at 275 cm\textsuperscript{-1} which lies between the 319 and 231 cm\textsuperscript{-1} frequencies of the HgCl\textsubscript{2} and CsHgCl\textsubscript{3} solids correspondingly. These observations indicate that upon melting CsHgCl\textsubscript{3} a new mercury "complex" is formed with coordination number higher than that in HgCl\textsubscript{2} (s) (i.e. 2) but lower than that in CsHgCl\textsubscript{3}(s) (i.e. 6). The strong polarized band observed in the Raman spectrum of KCl/HgCl (1/1) binary melt by Janz and James (9) at 282 cm\textsuperscript{-1} has been attributed to the symmetric stretching vibration of a planar HgCl\textsubscript{3}\textsuperscript{2-} complex. Most probably the 275 cm\textsuperscript{-1} band in molten CsHgCl\textsubscript{3} is due to the same species.

Cs\textsubscript{2}HgCl\textsubscript{4}: solid and melt.

The crystal structure of Cs\textsubscript{2}HgCl\textsubscript{4} is orthorhombic and isomorphous to \(\beta\)-K\textsubscript{2}SO\textsubscript{4} (10). Slightly distorted tetrahedra HgCl\textsubscript{4}\textsuperscript{2-} are present with one short (2.386 Å) and 3 longer (\(\simeq\)2.455 Å) Hg-Cl distances.

Figure 2 shows the Raman spectra of polycrystalline Cs\textsubscript{2}HgCl\textsubscript{4} from 300 to 663 K. The similarities of the four line spectrum of Cs\textsubscript{2}HgCl\textsubscript{4} solid at 300 K with the corresponding high temperature spectra of solid and liquid (Fig. 2) indicate a retention of the Hg coordination of the solid structure in the melt and leave little doubt about the assignments of these peaks to four lines expected for the tetrahedral HgCl\textsubscript{4}\textsuperscript{2-}. With increasing temperature all Raman bands shift to the red - the \(\nu_1\) from 275 cm\textsuperscript{-1} at 300 K is shifted to 269 cm\textsuperscript{-1} at 803 K - with a corresponding half width broadening. The high frequency Raman band of the solid at \(\simeq\)275 cm\textsuperscript{-1} (300 K) is attributed to the Hg-Cl vibrational frequency of the \(\nu_1\) symmetrical stretch of HgCl\textsubscript{4}\textsuperscript{2-} tetrahedra, the \(\nu_3\) being lower at 251 cm\textsuperscript{-1}. Such sequence of the \(\nu_1\) and \(\nu_3\) frequencies has been also reported before (11) for HgCl\textsubscript{4}\textsuperscript{2-} in the (Me\textsubscript{4}N\textsubscript{2})\textsubscript{2}HgCl\textsubscript{4} solid.

Cs\textsubscript{3}HgCl\textsubscript{5}: solid and melt.

An orthorhombic structure, with space group P\textsubscript{nma} (\(Z=4\)), has been reported (12) for the Cs\textsubscript{3}HgCl\textsubscript{5} crystal. The structure consists of Cs\textsuperscript{+}, Cl\textsuperscript{-} and distorted [HgCl\textsubscript{4}]\textsuperscript{2-} tetrahedral ions.

The Raman spectra of polycrystalline Cs\textsubscript{3}HgCl\textsubscript{5} at 77 and 298 K (Fig. 3) are in good agreement with factor group analysis based on the space group P\textsubscript{nma} (D\textsubscript{2h}\textsuperscript{8}) for the corresponding crystal. The similarity of the spectra for the high temperature solid (623 K) and melt (773 K) suggests that the vibrational modes of the HgCl\textsubscript{3}\textsuperscript{2-} tetrahedral species in the Cs\textsubscript{3}HgCl\textsubscript{5} solid are retained in the liquid.
Table I lists the main Raman frequencies observed in the HgCl$_2$-ACl (A=Li,Na,K,Cs) liquid mixtures at different representative compositions and temperatures. In Fig. 4 the Raman spectra of HgCl$_2$-CsCl liquid mixtures are shown at 873 K. The spectra of pure HgCl$_2$ melt was recently interpreted (7) in terms of a molecular liquid involving linear triatomic HgCl$_2$ type molecules and strong intermolecular forces. Progressive additions of CsCl, that is dissolving an ionic to a molecular liquid, give rise to an increase in the half width and a red shift of the $-310$ cm$^{-1}$ polarized band of pure HgCl$_2$ to 276 and 265 cm$^{-1}$ for $x_{\text{HgCl}_2}=0.5$ and 0.33 respectively. The low frequency depolarized "Rayleigh" wing of the HgCl$_2$-CsCl liquid mixtures possess a shoulder band in melts rich in either CsCl or HgCl$_2$. For intermediate composition $x_{\text{HgCl}_2}=0.5$ no shoulder band was observed. At compositions $x_{\text{HgCl}_2}\leq0.33$, the Raman peak positions are relatively constant, their intensities are proportional to the HgCl$_2$ mole fraction and the half width of the polarized band is narrower than that of the intermediate compositions. This implies that the predominant species in the CsCl rich region is the HgCl$_4^2$ and confirms our conclusions concerning the Cs$_2$HgCl$_4$ and Cs$_3$HgCl$_5$ solids and melts.

| Table I: Main Raman Frequencies in cm$^{-1}$ observed in the HgCl$_2$-ACl (A=Li,Na,K,Cs) liquid mixtures at different compositions and temperatures. |
|-----------------|-----------------|-----------------|
| A               | $x_{\text{HgCl}_2}=0.5$ | $x_{\text{HgCl}_2}=0.33$ | $x_{\text{HgCl}_2}=0.25$ |
|                 | $T$ (K)         | $T$ (K)         | $T$ (K)         |
| Li              | 294 873         | 289 873         | 282 873         |
| Na              | 286 923         | 281 923         | 279 973         |
| K               | 281 513         | 273 923         | 271 973         |
| Cs              | 276 873         | 265 873         | 262 873         |

Figure 5 shows the Raman spectra of HgCl$_2$/ACl (1/3) (A=Li,Na,K,Cs) liquid mixtures. The spectral features of the potassium and cesium systems are similar and confirm the presence of HgCl$_4^2$ species as suggested by Janz (9). The mixtures with LiCl and NaCl are characterized by a broad polarized Raman shoulder and the lack of the low frequency depolarized "Rayleigh" wing. The resemblance of the above characteristics to the Raman spectrum of CsHgCl$_3$ melt suggest that the HgCl$_3$ configurations are most probably stabilized in mixtures rich in NaCl or LiCl.
CONCLUSIONS

a) Upon melting CsHgCl$_3$, the octahedral configuration of the Hg in crystal changes and the melt microstructure is better characterized by a planar HgCl$_3$ type complex.
b) The Cs$_2$HgCl$_4$ and Cs$_3$HgCl$_5$ solid compounds melt with retention of the tetrahedral, HgCl$_4^{2-}$, configurations of the crystals.
c) In HgCl$_2$-ACl (A=Li, Na, K, Cs) molten salt mixtures, at high alkali halide concentration range, the HgCl$_4^{2-}$ and HgCl$_3$ configurations seem to be stabilized by the Cs$^+$, K$^+$ and Na$^+$, Li$^+$ ions respectively.

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Fig. 1: Raman spectra of polycrystalline and liquid CsHgCl₃; $\lambda_0=514.5$ nm, laser power (P) $\sim$ 50mW, Spectral Slit Width (SSW) $\sim$ 2 cm$^{-1}$, time constant ($\tau$) =0.1 s, Scan Rate (SR) = $0.5$ cm$^{-1}$ s$^{-1}$.

![Raman spectra of polycrystalline and liquid CsHgCl₃](image)

Fig. 2: Raman spectra of polycrystalline and liquid Cs₂HgCl₄. Spectra conditions as in Fig. 1.
Fig. 3: Raman spectra of polymeric stilbene and liquid Cs$_3$HgCl$_5$. Spectra conditions as in Fig. 1.

Fig. 4: Raman spectra of HgCl$_2$-CsCl liquid mixtures at 873 K. Spectra conditions as in Fig. 1.
Fig. 5: Raman spectra of 25% HgCl$_2$-75% AC$_i$ (A=Li, Na, K, Cs) liquid mixtures at $\sim$873 (A=Li, Cs) and $\sim$973 K (A=Na, K). Spectra conditions as in Fig. 1.