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The Nature of the Mixed Halides of Mercury(II)

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The material which has often been referred to as the mixed mercury(II) halide HgBrI was prepared using several different methods in order to investigate, the nature of the compound in the solid state. The Raman spectrum shows that "HgBrI" is a homogeneous equilibrium mixture of $HgBr_2$*–HgBrI–*HgI_2 *and cannot be prepared as a pure compound. Equimolar mixtures of the mercury(II) halides (*$HgCl_2$*,* $HgBr_2$*,* HgI_2*) were prepared in solvents, such as dioxane, tetrahydrofuran, acetone and isopropanol, in order to gain a more extensive picture of their solution equilibria. Relative intensities of Raman bands and their depolarization ratios suggest that these solutions are quite similar.*

Introduction

In 1869 the first report[1] of a mixed halide of mercury(II) *i.e.,* HgClBr, HgClI and HgBrI, appeared and since then about fifty papers have appeared discussing various aspects of these compounds. Most of the papers deal with the undisputed formation of these species as components of an equilibrium in the gas, molten, or solution phase.

The first work on the equilibrium solutions of mercury(II) halides was reported by Delwaulle and Francois in a series of papers.[2] The Raman spectra of equimolar mixtures of mercury(II) halides in methanolic, ethanolic and aqueous solutions revealed lines not ascribable to the original components and were assumed to result from the mixed halides. The intensity of the Raman lines was found to be proportional to the concentration of the species, but no attempt was made to calculate an equilibrium constant. However, Marcus described the formation of mixed mercury(II) halides by determining the distribution of mercury, iodine and bromine between benzene and aqueous solutions of mixed mercury(II) halides.[3] LogK for the reaction $HgX_2 + HgY_2 \rightleftarrows 2HgXY$ was reported to be 2.00 ± 0.50 for HgClBr, 1.75 ± 0.20 for HgClI, and 1.10 ± 0.20 for HgBrI. Calculations of the formation constants of mixed mercury(II)halides from the parent halides made on the basis of a "polarized ion" model were found to agree well with previous experimental results.[4] Equilibrium studics of the formation of mixed mercury(II) halides in perchloric acid medium using spectrophotomeric means gave somewhat lower values for logK, but it has been suggested that this is due to the interaction of the dipole of the mixed species with the solvent.[5]

Evidence of mixed halides of mercury(II) as equilibrium components in the gas phase was reported in 1943[6] and more recently studied by Raman spectroscopy.[7] The spectra of the mixed halides are largely temperature independent in the gaseous state, thus no equilibrium data could be calculated. Similar studies have been made of mixed mercury(II) halides in the molten state by combining the two molten mercury(II) halides to form an equilibrium mixture.[8,9] Both the gaseous and molten state studies indicate that the mixed halides are linear triatomic molecules like the pure halides.

In the solid state, however, several papers suggest the existence of pure mixed mercury(II) halides.[1,10–14] In fact, the primary reference on physical and chemical properties of materials lists data for presumably pure HgBrI.[15] Criteria for the solid compound have been mercury analyses and the fact that, in the case of HgBrI, a yellow crystalline compound of constant composition is obtainable upon sublimation. The earliest preparation of a solid mixed mercury(II) halide used the method of halide exchange between $HgBr_2$ and several alkyl iodides to make HgBrI.[1] Recent work indicates that HgClI and HgBrI can be prepared in the solid state by the reaction of a solid mercury(I) halide with iodine.[12,13] HgClI was reported to be unstable with respect to disproportionation to $HgCl_2$ and HgI_2, but HgBrI was found to be stable and should be suitable for more intensive study.

In this project, the nature of solid HgBrI as prepared by the various known synthetic routes was explored by Raman spectroscopy and the results compared to the gaseous and molten data. The Raman spectra of equilibrated solutions of mixed halides of mercury(II) were also recorded in the hope of gaining a more extensive picture of the solution properties of these compounds.

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Experimental

Materials

All solid materials used were of reagent grade and were not purified further. The solvents used in the Raman studies were spectral grade, all others were reagent grade.

Bromoiodomercury(II)

A method similar to that described by Rastogi and Dubey[13] was used to prepare HgBrI. Hg_2Br_2 (10.00 g) and I_2 (4.52 g) were ground together with a mortar and pestal until homogeneously dispersed and placed in a stoppered Erlenmeyer flask. After several days the crude material from the reaction showed a definite yellow color. This crude product was washed with CCl_4 to remove unreacted I_2 and the remaining product was dissolved in a complexing solvent, such as dioxane or ethanol, to dissolve mercury(II) salts. The solution was filtered to remove unreacted insoluble Hg_2Br_2. Upon evaporation of the solvent a yellow product which was thought to be "HgBrI" was obtained. Recrystallization was effected from ethanol. When dioxane was used as the solvent the colorless dioxanate adduct of the product was isolated. It could be converted to the yellow "HgBrI" by evacuation and gentle heating of the product. When this material was sublimed under vacuum, a yellow crystalline solid was obtained.

HgBrI was also prepared using the method of halide exchange between $HgBr_2$ and ethyl iodide.[1] $HgBr_2$ (5.7 g) are dissolved in a minimum amount of acetone and 1.30 ml of ethyl iodide are added. The crude product was obtained upon evaporation of the solvent, collected and sublimed under vacuum.

Solution Studies

By far the most common method of preparing mixed mercury(II) halides has been to prepare solutions containing equimolar amounts of the mercury(II) halides. Solutions were prepared by dissolving equimolar amounts of two mercury(II) halides in dioxane, tetrahydrofuran (THF), acetone, or isopropanol (*i*-PrOH) in a 25 ml volumetric flask. The solvents chosen and concentrations of the solutions depended on the solubility of the halides in the solvents and whether or not the solvent absorptions interfered with the Hg–X modes. Dioxane and THF solutions contained 0.597 g of $HgCl_2$, 0.792 g of $HgBr_2$, and 1.000 g of HgI_2. The *i*-PrOH solutions contained 0.298 g of $HgCl_2$, 0.396 g of $HgBr_2$, and 0.500 g of HgI_2. The acetone solution contained 0.452 g of $HgCl_2$ and 0.600 g of $HgBr_2$.

Raman Spectra

The Raman spectra were recorded on a Spex Ramalog laser spectrometer with photon counting and 5145 Å excitation. "HgBrI" as a solid decomposes somewhat at this wavelength so the compound was rotated in the laser beam during spectral recording. The samples were run in sealed capillary tubes. All spectra were run at room temperature and should be accurate to ± 2 cm^{-1}.

Results and Discussion

The Raman data for the mixed halides of mercury(II), including relative intensities and polarization ratios, $\varrho = \frac{I_{\parallel}}{I_{\perp}}$, of stretching vibrations of mercury-halogen bonds are summarized in Table I. The Raman spectrum of "HgBrI" after sublimation and $HgBr_2$–HgI_2 in dioxane solution are reproduced in Figures 1 and 2. The bands reported are due only to the stretching modes, but several low frequency bending, and lattice modes are also observed in the solid state.

Mixed mercury(II) halides, being linear triatomic molecules, are assigned to the $C_{\infty v}$ point group. Thus, the pseudo-symmetric stretch (ν_1) and the pseudo-asymmetric stretch (ν_3) both have Σ^+ symmetry and

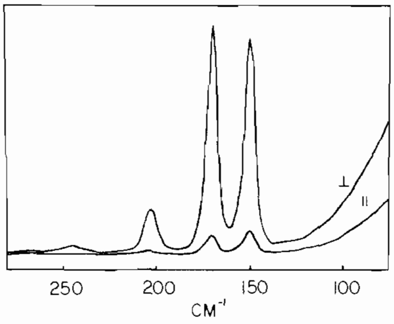

Figure 1. Raman spectrum of an equimolar mixture of $HgBr_2$–HgI_2 in dioxane showing depolarization properties. The spectral slits were at 150 cm^{-1} and the laser power was 175 mW.

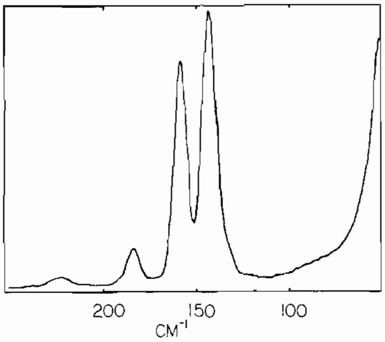

Figure 2. Raman spectrum of solid "HgBrI".

TABLE I. Raman Shifts, Intensities and Depolarization Ratios, ϱ, of Stretching Vibrations in HgX_2–HgY_2 Mixtures in Various Forms.

	Bond	$\nu(cm^{-1})$[a]					
		THF	*i*-Propanol	Acetone	Dioxane		Pure Solid
					Soln	Solid	
$HgBr_2$–HgBrI–HgI_2	$HgI_2(\nu_1)$	149(9.4)	151(8.8)		148(8.9)	143(9.9)	139(10.0)
	ϱ	0.12	0.11		0.10		
	HgI(Br)	169(10.0)	173(10.0)		168(10.0)	158(10.0)	155(7.5)
	ϱ	0.11	0.10		0.09		
	$HgBr_2(\nu_1)$	202(1.7)	205(2.0)		201(2.3)	185(2.4)	181(1.1)
	ϱ	0.10	0.05		0.10		
	HgBr(I)	241(0.6)	246(0.4)		243(0.5)	230(0.3)	223(0.3)
	ϱ	0.17	–		0.15		
$HgCl_2$–HgClI–HgI_2	$HgI_2(\nu_1)$	148(10.0)			149(10.0)		
	ϱ	0.18			0.14		
	HgI(Cl)	184(6.0)			185(5.5)		
	ϱ	0.15			0.12		
	$HgCl_2(\nu_1)$	322(1.0)			320(0.7)		
	ϱ	0.10			0.09		
	HgCl(I)	335(1.0)			336(0.8)		
	ϱ	0.10			0.10		
$HgCl_2$–HgClBr–$HgBr_2$	$HgBr_2(\nu_1)$	205(9.3)	207(8.8)	211(10.0)	204(10.0)		
	ϱ	0.12	0.11	0.09	0.11		
	HgBr(Cl)	233(10.0)	233(10.0)	239(10.0)	233(7.5)		
	ϱ	0.09	0.08	0.07	0.10		
	$HgCl_2(\nu_1)$	322(3.0)	325(3.6)	331(5.0)	322(2.6)		
	ϱ	0.06	0.11	0.08	0.06		
	HgCl(Br)	347(2.1)	346(2.0)	356(3.5)	347(2.0)		
	ϱ	0.07	0.10	0.08	0.08		

[a] Parenthetical numbers are intensities based on a scale of 0.0 to 10.0.

are Raman active and polarized. However, a Raman spectrum of the crude material from the Hg_2Br_2–I_2 reaction reveals five bands. Upon recrystallization one of these bands disappears and another becomes considerably less intense. These bands are attributable to unreacted Hg_2Br_2 and are the same as the bands observed in the Raman spectrum of pure $HgBr_2$.[16] One of the Hg_2Br_2 bands is very close in frequency to the $HgBr_2$ mode. Two of the remaining four bands occur at frequencies quite close to those reported for pure $HgBr_2$ and pure HgI_2. Both of these mercury(II) halides are linear triatomic molecules in the solid state and thus belong to the $D_{\infty h}$ point group. A polarized symmetric stretch (ν_1) of Σ_g^+ symmetry will be present for them both, while the Raman inactive asymmetric stretch (ν_3) of Σ_g^- symmetry will be absent. Using this information one can assign the two peaks in the Raman spectrum of solid "HgBrI" at 139 cm^{-1} and 181 cm^{-1} to $HgI_2(\nu_1)$ and $HgBr_2(\nu_1)$ respectively. The remaining two peaks result from the mixed species and are assigned to HgI(Br) at 155 cm^{-1} and HgBr(I) at 223 cm^{-1}. Thus, the sublimed yellow material, which has been referred to as "HgBrI", actually contains $HgBr_2$, HgBrI, and HgI_2 in roughly similar amounts according to the Raman spectrum.

Powder diffraction data[14] for "HgBrI" have been reindexed[17] and found to give approximately the mean cell dimensions of pure $HgBr_2$ and yellow HgI_2. The Raman spectrum confirms that, rather than a pure compound, "HgBrI" is a homogeneous lattice mixture of $HgBr_2$, HgBrI, and HgI_2 such that the percentage of mercury in the mixture is close to that of idealized HgBrI. The manner in which the "HgBrI" is prepared seems to make no difference. The Raman spectrum of HgBrI prepared from the halide exchange reaction between $HgBr_2$ in acetone and ethyl iodide is similar to that obtained by the Hg_2Br_2–I_2 route. Interestingly, this equilibrium mixture can be sublimed and recrystallized intact to give a yellow crystalline material whose composition does not change.

The Raman shift of the symmetric stretch in the pure mercury(II) halides occurs at the lowest frequency in the solid state,[18,19] slightly higher in the molten state and much higher in the gaseous state.[7] Table II con-

TABLE II. Raman Shifts of Stretching Vibrations of the $HgBr_2$–HgI_2 Mixture in Various Forms.

Bond	$\nu(cm^{-1})$		
	Solid	Molten[9]	Gaseous[7]
$HgI_2(\nu_1)$	139	146	167
HgI(Br)	155	167	182
$HgBr_2(\nu_1)$	181	195	229
HgBr(I)	223	229	266

tains the values found for the stretching vibrations in solid "HgBrI" along with those reported for $HgBr_2$–HgBrI–HgI_2 in the molten and gaseous states. The ordering of the Raman shifts from lowest to highest follows the same trend.

The colorless solid dioxanate complex of "HgBrI" was also isolated and its Raman spectrum recorded. All bands of the "HgBrI" dioxanate solid were found to be shifted to lower frequencies by about the same amount when compared to the dioxane solution, but are similar to those of solid "HgBrI". The same behavior is noted when the shifts for the solid $HgBr_2$ and HgI_2 dioxanate adducts and their dioxane solutions are compared.[20]

As previously mentioned the Raman spectra of HgX_2–HgY_2 mixtures have been reported in various solvents.[2] To give a more extensive picture of the solution properties, equimolar mixtures of the various mercury(II) halides were prepared and their Raman spectra recorded. The results, including the depolarization ratios, ϱ, appear in Table I. Intensity comparisons indicate it would not be entirely valid to calculate equilibrium constants from the band intensities because they are not solely a function of concentration. Changes in bond polarization due to solvent interactions also seem to be important. However, the relative intensities and depolarization ratios are fairly constant in the solutions studied, suggesting a high degree of similarity among the solutions. All the depolarization ratios are less than 3/4 as predicted for vibrations belonging to totally symmetric representations such as Σ^+ and Σ_g^+.

The Raman intensities follow the trend: HgI > HgBr > HgCl. This is as expected since polarizability is related to volume change and the ease of polarizing the atoms. Calculations have shown[21] the amount of ionic character in the mercury–halogen bond is least for HgI and greatest for HgCl, which agrees with the Raman spectra.

Presumably the nature of the interaction between the solvent and the mercury(II) species in solution can account for various trends observed in the Raman spectra. For example, changes in the depolarization ratios may correspond to some differences in the solvent–solute interaction. A comparison of the dielectric constant of the solvent and the depolarization ratio was made using the dielectric constants: acetone, 20.7, *i*-PrOH, 18.3, THF, 7.58, dioxane, 2.2.[15] Comparing values for the $HgCl_2$–HgClBr–$HgBr_2$ system, the only one investigated in all of these solvents, shows no strong correlation. It is possible that a more thorough investigation of HgXY depolarization ratios in many other solvents might show a correlation, but such a trend may not exist since the dielectric constant measures a bulk property of the solvent, whereas the ϱ values are likely to depend more on the nature of the solvent donor site.

The vibrational frequencies for mercury(II) halides range from $HgI_2(\nu_1)$, the lowest, to $HgCl_2(\nu_1)$, the highest which is due mostly to a mass effect. For IHg–X the same trend is also observed. As X goes from I to Cl the vibrational frequency of the HgI bond decreases. However, a different trend effect is found in HgBr and HgCl bonds indicating other factors, such as bond covalency changes are complicating features in this generalization.

Many other routes to the preparation of the mixed halides of mercury(II) certainly exist, but it is doubtful that a pure compound can be isolated from any because any solution, melt, or gas phase manipulation would result in a rapid disproportionation to an equilibrium mixture. Thus, reports of the existence and properties of pure mixed halides of mercury(II) appear to be incorrect.

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