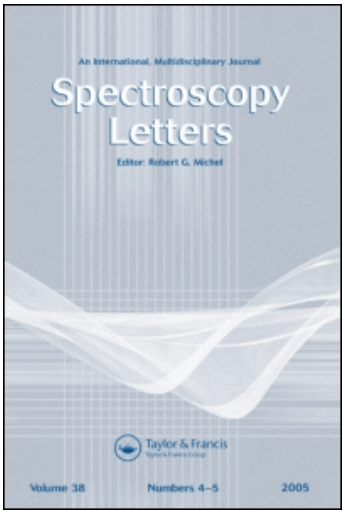

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INFRARED AND RAMAN SPECTRA OF SOME IODIDE-BRIDGED COMPLEXES OF MERCURY (II)

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Key Words: Iodide-bridged complexes of mercury (II), infrared and Raman Spectra, mixed binuclear halogen-bridged species.

ABSTRACT

The IR and Raman Spectra of pentaiododimercurate (II) and octaiodotrimercurate (II) anionic complexes have been obtained in the solid state and interpreted in terms of halogen-bridged structures. Spectroscopic and chemical evidences support a dimeric structure for the pentaiododimercurate (II) anion.

The addition of $HgBr_2$ and HgI_2 to tetraiodocadmate (II), mercurate (II) and tetrabromocadmate (II) species have also been studied. The vibrational spectra also support halogen-bridged structures for these new mixed binuclear complexes.

INTRODUCTION

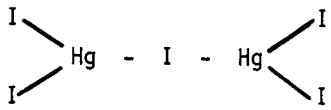
In 1961, Deacon and West reported the aqueous decomposition of a number of polinuclear species of mercury (II) derived from mercury diiodide (1). The compounds MHg_2I_5 and $M_2Hg_3I_8$ where M is tetramethylammonium, pyridinium or tetramethylphosphonium, decompose in boiling aqueous solutions to produce HgI_2, I^- and the corresponding organic cation. The Raman spectra of acetone solutions of these species show bands located at 134 and 150 cm^{-1}.

In the $Me_4N|Hg_2I_5|$ a medium intensity emission at 142 cm^{-1} was also observed. Hooper and James (2) assigned the former two bands to the symmetric stretching modes of the HgI_3^- and HgI_2 species, implying that in acetone solution the polynuclear halogen-bridged species are broken down as follows:

$$Me_4N|Hg_2I_5| \longrightarrow Me_4N^+ + HgI_3^- + HgI_2$$

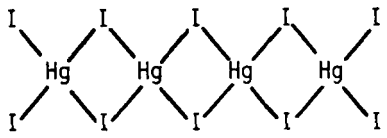
$$(Me_4N)_2|Hg_3I_8| \longrightarrow 2Me_4N^+ + 2HgI_3^- + HgI_2$$

The band at 142 cm^{-1} was assigned to the terminal symmetric stretching mode of the $Hg_2I_5^-$ anion also present in solution and whose structure was proposed to be:



(A)

Perlepes et al (3) have suggested that the pentaiododimercurate (II) complex could also have a structure of the type B, i.e., similar to that



(B)

certainly present in the $Hg_3I_8^=$ species. However, based on some few IR bands they conclude that structure type A is more likely to occur for this anion.

In an attempt to remove the ambiguity in the structure of the pentaiododimercurate (II) anion and as a part of our continuing interest in the mercury-halogen systems (4-6), we have reinvestigated these polynuclear species, namely, $Hg_2I_5^-$ and $Hg_3H_8^=$ as salts of tetramethylammonium. We have also studied the addition of $HgBr_2$ and HgI_2 to the tetrahedral cadminium (II)-halide complexes and obtained some heterobinuclear halogen-bridged species.

EXPERIMENTAL

a) Preparative

The salts $Me_4N|Hg_2I_5|$ and $(Me_4N)_2|Hg_3I_8|$ were prepared by a standard method. The stoichiometric amount of HgI_2 was suspended in a hot solution of tetramethylammonium iodide in acetone. The suspension was stirred for one hour and the yellow solution allowed to evaporate slowly at room temperature. In both cases yellow crystals were obtained and recrystallized twice from the same solvent.

The salts $(Me_4N)_2|CdHgI_6|$ and $(Me_4N)_2|CdHgI_4Br_2|$ were prepared by reacting the stoichiometric amount of $(Me_4N)_2|CdI_4|$ with HgI_2 or $HgBr_2$ in acetone. The resulting solution was allowed to evaporate to dryness and the yellow crystals recrystallized twice from the same solvent. The $(Me_4N)_2|CdHgBr_4I_2|$ was obtained by the same procedure but a mixture of EtOH/acetone was used.

In all cases the analytical data agree well with the formulae given above.

b) Physical Measurements

The Raman spectra were obtained as described elsewhere (7). The spectra were observed either in powdered or single crystal samples. In the latter, the orientation of the specimen was achieved by maximizing the intensity of a previously chosen band.

The IR spectra were recorded on a IFT-88 Brucker spectrophotometer using polyethylene powder to produce the pellets.

RESULTS AND DISCUSSION

The IR and Raman Spectra of the octaiododimercurate (II) complex (see table 1) shows four mercury-iodide terminal stretching modes in keeping with the halogen-bridged suggested structure (2,3). The mercury-iodide bridging modes are not all observed probably due to accidental coincidences. In fact, the vibrational spectra shows a band at c.a. 125 cm^{-1} that can be assigned to these modes. It is worthnoting that in the Hg-I terminal stretching region (130-185 cm^{-1}) almost a complete exclussion of the IR and Raman bands is

Table 1

IR and Raman Spectra (cm^{-1}) of the $(Me_4N)_2|Hg_3I_8|$ and $Me_4N|Hg_2I_5|$ Solids ($Me_4N = (CH_3)_4N^+$)

$(Me_4N)_2\|Hg_3I_8\|$		$Me_4N\|Hg_2I_5\|$		Assignment[a]
IR	Raman	IR	Raman	
	81vw			
			90m	B
			112m	B
		115ms		B
125ms	124s		123s	B
		128ms		B
	139vs		139vs	T
145s		144ms		T
161s		160s		T
			179m	T
185s	183vw			T

a) B = Bridging; T = terminal stretching modes

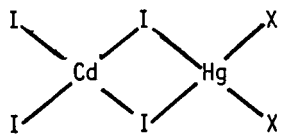
observed implying that, though the molecular symmetry is C_{2v}, the factor group is probably a centrosymmetric one.

The IR spectrum of the pentaiodimercurate (II) species shows two bands located at 144 and 160 cm^{-1}, whereas the Raman spectrum exhibits another two bands at 139 and 179 cm^{-1}. These bands correspond to the Hg-I terminal stretching modes. Those detected between

90 and 128 cm^{-1} have been assigned to the bridging modes of the dimeric $Hg_2I_5^-$ anion.

The expected number of terminal (T) and bridging (B) stretching modes for type A and B structures of this anion are 4T + 2B and 4T + 12B respectively. In the vibrational spectra of the $Hg_2I_5^-$ species at least five bridging stretching frequencies are observed in better agreement with a type B structure for this anionic complex. Additional support for such structure comes from the reaction of stoichiometric amounts (1:1) of $Me_4NHg_2I_5$ and 2,2'-bipyridyl in acetone. If the pentaiododimercurate (II) complex possesses a type A structure, the reaction products will be $Me_4N|HgI_3|$ and $|Hg(bipy)I_2|$, whereas for a type B structure $|Hg(bipy)I_2|$ and $(Me_4N)|Hg_3I_8|$ can be obtained. In fact, these latter two products were isolated from the above reactions. The $(Me_4N)|Hg_3I_8|$ was identified by its melting point, quantitative elemental analysis and Raman spectra.

Since the pentaiodo and octaiodo mercurate (II) species can also be prepared from the reaction of mercury (II) iodide with tri and tetraiodomercurate (II) complexes respectively, we have also explored the addition of HgI_2 and $HgBr_2$ to the tetrahedral CdI_4^{2-} and $CdBr_4^{2-}$ anionic complexes. The reaction of the former with either HgI_2 or $HgBr_2$ produces the anionic species:



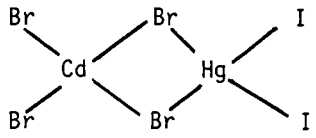
X = Br or I

Table 2

IR and Raman Spectra of some Mixed Binuclear Halogen-Bridged Complexes

$(Me_4N)_2\|CdHgBr_4I_2\|$			$(Me_4N)_2\|CdHgI_4Br_2\|$			$(Me_4N)_2\|CdHgI_6\|$		
IR	Raman	Assignment	IR	Raman	Assignment	IR	Raman	Assignment
	97w			109w			103w	
132s	135vs	$Hg\text{-}I_T$		135s	$Cd\text{-}I_T$	129s	127m	$Hg\text{-}I_T$
							132vs	$Hg\text{-}I_T$
144vs	144s	$Hg\text{-}I_T$	149vs	144vs	$Cd\text{-}I_T$		138ms	$Cd\text{-}I_T$
158vs		$Cd\text{-}Br_T$		159w	$Hg\text{-}Br_T$	153vs	153vs	$Cd\text{-}I_T$
	173w	$Cd\text{-}Br_T$	177vs	173w	$Hg\text{-}Br_T$			
184s								

whereas the latter reacts with HgI_2 only, to yield



The IR and Raman Spectra of these species are given in Table 2.

All three compounds show a strong band at ca. 135 cm^{-1} which has been assigned either to the Hg-I_T or Cd-I_T stretching modes. A similar situation is observed for the band at ca. 145 cm^{-1}, though this band is shifted to 138 cm^{-1} in the $CdHgI_6^{2-}$ species. The assignment of the stretching frequencies is not straightforward in these anionic species since the CdI_4^{2-} and HgI_4^{2-} complex show bands at 118 and 145 and 116 and 134 cm^{-1} respectively. In the $CdHgBr_4I_2^{2-}$ anion the bridging Cd-Br frequencies must lie in the same region of the Hg-I terminal. This implies that in these mixed binuclear species the Hg-I and Cd-I termal stretching modes are also very close one to another. Hence the assignment given in Table 2 is tentative only.

Finally, it is interesting to note that attempts to insert $HgCl_2$ into either $HgCl_4^{2-}$ or $CdCl_4^{2-}$ failed.

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