Compounds of Complex Halo and Pseudohalo Acids of the Group IIB Metals, Part V [1]

Preparative and Spectroscopic Studies of the $[Hg_2I_5]^-$, $[Hg_2I_6]^{2-}$ and $[Hg_3I_8]^{2-}$ Ions

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The preparations of new compounds, containing the complex anions $[Hg_2I_5]^-$, $[Hg_2I_6]^{2-}$ and $[Hg_3I_8]^{2-}$, are reported.

Distorted iodine-bridged configurations are proposed for the complexes in the solid state, utilising analyses, X-ray powder patterns, molar conductance measurements and spectral (IR, UV) data.

Introduction

Previous efforts to prepare halogen-bridged anionic complexes of Hg(II) by the method of "etherohalogenosis" [2] met with failure in this department. Recently, however, we were able to isolate three new salts having the $[Hg_2I_5]^-$, $[Hg_2I_6]^{2-}$ and $[Hg_3I_8]^{2-}$ ions; the present paper reports the preparation and characterization of these salts. Very few preparative and spectroscopic studies have been made on iodomercurate(II) complexes with dimeric or polymeric anionic structures [3–6]. It was pointed out by Deacon [7] that no cation appears to give both $[Hg_2I_5]^-$ and $[Hg_3I_8]^{2-}$ complex anions.

Experimental

High purity materials were used throughout this work. The analyses and physicochemical measurements were carried out as previously reported [8–10].

$[(3\text{-pic})_2H]_2[Hg_2I_6]$

The preparation of this complex was analogous to that of $HHgI_3 \cdot 2\,Py$ [11] (Py = pyridine and 3-pic = 3-methyl pyridine).

$(QuH)[Hg_2I_5]$

Quantities of QuHI (Qu = quinoline) and HgI_2 in a molar ratio 1:2 were dissolved in warm absolute acetone. The product was obtained by evaporation of the solvent until crystallization began.

$(QuH)_2[Hg_3I_8]$

Quantities of $(QuH)_2[HgI_4]$ and HgI_2 in a molar ratio 1:2 were heated in absolute acetone. The reaction mixture was refluxed, until a clear solution was obtained. Stirring was continued at 50 °C for 30 min. After cooling to room temperature, the solution yielded the octaiodotrimercurate(II) salt as microcrystals (method A).

Quinolinium tri-iodomercurate(II) [1] was heated as a suspension in water (40 ml) at 85–90 °C, until a melt began to form on the bottom of the reaction vessel (10 min). The melt was separated from the solution. On cooling, crystals were deposited from the solution. This crystalline material was found to be the octaiodotrimercurate(II) complex (31%). The solidified melt consisted mainly of the same complex, together with some HgI_2 (method B).

Results and Discussion

The analytical results and some physicochemical data are given in Table I. The crystalline complexes are stable in the atmosphere, insoluble in nonpolar solvents, somewhat soluble in alcohols and soluble in CH_3NO_2, DMF and DMSO; they are decomposed by dilute mineral acids. The X-ray powder patterns of the complexes are different; all patterns suggest, by the multitude of the reflections, that the compounds formed are of low symmetry.

The octaiodotrimercurate(II) complex decomposes in water to form insoluble mercuric iodide:

$$(QuH)_2[Hg_3I_8] \xrightarrow[95\,°C]{H_2O} 3\,HgI_2 + 2\,QuH^+ + 2\,I^-.$$

The UV spectrum of the picolinium complex in EtOH (400–220 nm), in addition to the absorption maxima due to the well known $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, shows three maxima at 301, 333 and

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360 nm; these three peaks appear at about the same positions in DMF and DMSO. The 301 and 333 nm maxima indicate the presence of solvated HgI_3^- ions [12] in solution. The HgI_3^- ion has 24 valency electrons and these fill the orbitals up to and including $1a_2$. The $(1a_2)^2$ ground state for both planar and pyramidal ions is $^1A_1$. The peak at 301 nm is assigned to the electron excitation to the $4a_1$ orbital from the 4e one. The spin forbidden transition $^1A_1 \rightarrow {}^3E$ is made partially allowable by the mixing of the ^3E and ^1E states *via* spin-orbid coupling, giving the small low energy peak at 333 nm. The *ca.* 360 nm maximum is assigned to the $\pi_g \rightarrow \sigma_u^*$ transition of the I_3^- ion [13]. The spectra of the quinolinium complexes show absorption maxima at 223, 226, 231, 271, 276, 282, 287, 293, 300, 305 and 313 nm; these are due to electronic transitions of quinoline, since they appear in the spectra of Qu and QuHI. The spectrum of $(QuH)_2[Hg_3I_8]$ exhibits the additional maximum at 360 nm, which appears clearly reinforced when the spectrum is recorded 2–3 h after the preparation of the solution. The absence of the above transition from the spectrum of (QuH)$[Hg_2I_5]$ shows its greater stability in EtOH; this begins to appear after approximately 3 h, for a 10^{-4} M solution.

The complexes have IR spectra (4000–250 cm^{-1}), in the solid state, indicative of the absence of lattice or coordinated organic base [14] and of the existence of BH^+ ions involved in hydrogen bridging [15]. In the picolinium compound the counterion appears to be the [3-pic H 3-pic]$^+$ cation. Several complexes with $(N\text{–}H \text{ ---} N)^+$ bonding have attracted attention recently [16, 17].

The Far-IR spectra (Table II) of the prepared complexes give an insight into the structure and the bonding in the solid state. Only features at < 250 cm^{-1} are listed, since it was clear that no fundamentals of the complex anions occurred above this wavenumber.

The spectrum of the picolinium complex, as a solid, shows four bands in the region appropriate to HgI stretching. This number of stretching vibrations is, of course, much greater than that to be

Table I. Analytical results, yields, colors and decomposition temperatures for the prepared complexes.

Compound	[%]	H^+	Hg	I	B	Yield^a [%]	Color	Decomp. temp. [°C]
$[(3\text{-pic})_2H]_2[Hg_2I_6]^c$	Calcd	0.13	26.10	49.53	24.23	91	pale yellow	117–122
	Found	0.14	26.37	49.89	23.97			
$(QuH)[Hg_2I_5]$	Calcd	0.09	34.41	54.42	11.08	89	brown	179–183
	Found	0.10	34.49	54.21	11.40			
$(QuH)_2[Hg_3I_8]$	Calcd	0.11	32.05	54.08	13.76	71^b	yellow	117–120
	Found	0.11	31.63	54.37	14.06			

B = 3-pic, Qu; [a] based on the metal; [b] method A; [c] the values of molar conductance for *ca.* 10^{-3} M solutions at 25 °C are: $\Lambda_M(CH_3NO_2) = 87$, $\Lambda_M(DMF) = 76$ and $\Lambda_M(DMSO) = 34$ S cm^2 mol^{-1} (the compound was assumed to be monomeric in solution).

Table II. Far-IR^a assignments (250–50 cm^{-1}) of diagnostic absorption bands for the iodomercurate(II) complexes in the solid state.

Assignment	$[(3\text{-pic})_2H]_2[Hg_2I_6]$	$(QuH)[Hg_2I_5]$	$HgI_2^{b,c}$	$(QuH)_2[Hg_3I_8]$	$(Qu_2H)[HgI_3]^{b,d}$
$\nu(HgI_2)$			200	210 m	
$\nu_{as}(Hg\text{–}I)_t$	154 s	178 s		154 s	151 m
$\nu_s(Hg\text{–}I)_t$	138 s	142 m		126 s	130 s
$\nu(HgI)_b$	103 m, 96 mbr	115 m, 98 m		103 m	101 m
				88 m	91 mbr
$\delta(IHgI)$	64 m, 57 m, 52 sh	61 mbr		66 m	63 m
				54 m	54 w

[a] Data obtained at room temperature; [b] presented for correlation purposes; [c] from ref. [4]; [d] from ref. [1]. ν_s = symmetric stretching, ν_{as} = antisymmetric stretching, δ = deformation, t = terminal, b = bridging, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

expected for a $[HgI_3]^-$ ion of any shape, but is in accordance with predictions for a D_{2h} dimeric anion $[Hg_2I_6]^{2-}$ which, based on tetrahedral geometry around the metal, should show four IR-active ($B_{1u} + B_{2u} + 2B_{3u}$) modes [18]. The possibility of the $[Hg_2I_6]^{2-}$ system being a mixture can be ruled out on the ground that this does not show bands at the same wavenumbers as $[HgI_4]^{2-}$ [4] and $HgI_2 \cdot 2L$ [19].

The band at 210 cm^{-1} for $(QuH)_2[Hg_3I_8]$ is comparable in energy with that of yellow HgI_2 (200 cm^{-1}) [20]. This is a good evidence for a "lattice" HgI_2 in the complex. The remaining spectral features show a marked similarity to the spectra of $[(3\text{-pic})_2H]_2[Hg_2I_6]$ and $(Qu_2H)[HgI_3]$ [1]. This correlation is shown in Table II. So, the spectral results indicate that the prepared solid should be better written $(QuH)_2[(HgI_3)_2] \cdot HgI_2$. Structures based on a chain or dimeric unit with a "lattice" HgI_2 can be assigned. In the spectrum of the octaiodotrimercurate (II) salt the vibration assignable to the "lattice" HgI_2 is at higher energy than that observed for solid HgI_2. This can be explained by the assumption that in the complex the "lattice" HgI_2, in which the mercury is in a distorted octahedral environment of iodine atoms, is far less the subject of interatomic interactions than the HgI_2 molecules in crystalline mercuric iodide where the Hg(II) atom is also in an octahedral environment. This would result in a bond shortening in the "lattice" HgI_2 [4].

The IR stretch at 178 cm^{-1} in the spectrum of $(QuH)[Hg_2H_5]$ is higher than the stretch for the picolinium complex (154 cm^{-1}) and lower than the asymmetric stretch of yellow HgI_2 (200 cm^{-1}). Thus the nature of this Hg–I bond must be somewhere intermediate between the bond nature in yellow HgI_2 and $[Hg_2I_6]^{2-}$. Possible coordination environments for the Hg(II) atom in $[Hg_2I_5]^-$ are shown in Fig. 1. If an environment similar to that in Fig. 1a is applicable, then the structure would most likely be based on a $[Hg_4I_{10}]^{2-}$ unit. However, the spectral results favor the arrangement indicated in Fig. 1b, where HgI_2 units are joined by a bridging iodine with possible other iodines at long distances above and below the plane.

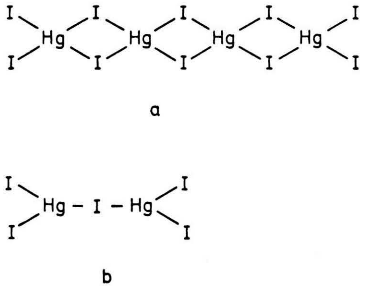

Fig. 1. Possible arrangements for $[Hg_2I_5]^-$.

The fact that for the picolinum complex the predominant species in solution (EtOH, DMF, DMSO) is the solvated HgI_3^- ion is attributed to the reaction:

$$[(3\text{-pic})_2H]_2[Hg_2I_6] \xrightarrow{\text{solvent}} 2[HgI_3 \cdot x\text{solvent}]^- + 2(3\text{-picH})^+ + 2(3\text{-pic}).$$

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