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Some Mixed Halogenomercurate(II) Anionic Complexes. Vibrational Spectra and Structure

J. G. CONTRERAS* and G. V. SEGUEL

Departamento de Química, Universidad de Concepción, Casilla, 3-C, Concepción, Chile

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Anionic complexes of the type $HgCl_2X^-$ where X = Br or I have been prepared as salts of tetrapropylammonium cation. IR and Raman spectra are interpreted in terms of halogen-bridged dimeric species, in keeping with molecular weight determinations. Vibrational spectra and reactions of these complexes with 2,2'-dipyridyl allow us to infer a C_{2v} (type A) structure for these species.

Introduction

The structure of the trihalogenomercurate(II) complexes have been the subject of a number of X-ray diffraction and spectroscopic studies [1–6].

The trichloromercurate(II) anion shows at least four types of structures, namely, polymeric based on $HgCl_6$ octahedra [1], trigonal planar [7], trigonal bipyramidal [8] and dimeric halogen bridged [6]. In fact, the latter has been found for all trihalogenomercurate(II) [4, 6, 9] as well as for the diiodohalogenomercurate(II) anions [10] as salts of tetrapropylammonium.

As a part of our continued interest in halogeno complexes of non-transition metals [11–16] and on mercury in particular, we have prepared and characterized two new species derived from the trichloromercurate(II) anion by halogen substitution. Accordingly, we have obtained the far-ir and Raman spectra of the dichlorobromo and dichloroiodomercurate(II) anions as salts of tetrapropylammonium. In order to bring out more evidence on the nature of the bridging halogens, some chemical reactions of these species with 2,2'-dipyridyl(dipy) have also been carried out.

Experimental

Preparative

i. $(C_3H_7)_4NHgCl_2X$ (X = Br or I)

These compounds were prepared by dissolving mercury(II) chloride in an ethanolic solution of the stoichiometric amount of the appropriate tetrapropylammonium salt. The reaction mixture was left with stirring for 1–2 hr and the precipitate filtered off, washed with ethanol and dried at *ca.* 60 °C. The solids were recrystallized twice from acetonitrile.

Anal. Calc. for $(C_3H_7)_4NHgCl_2Br$: C, 26.8; H, 5.2; N, 2.6; Hg, 37.4; found: C, 26.9; H, 5.3; N, 2.9; Hg, 37.6.

Anal. Calc. for $(C_3H_7)_4NHgCl_2I$: C, 24.6; H, 4.6; N, 2.4; Hg, 34.3; found: C, 24.1; H, 4.8; N, 2.5; Hg, 34.1.

ii. Reactions with 2,2'-dipyridyl (dipy)

A solution of the corresponding $HgCl_2X^-$ complex (X = Br or I) in acetonitrile was added to another containing the stoichiometric amount of dipy. A white precipitate formed immediately, and was filtered off, washed with acetonitrile and dried at *ca.* 60 °C.

Anal. Calc. for $HgClBr\,C_{10}H_8N_2$: C, 25.4; H, 1.7; N, 6.0; Hg, 42.5; found: C, 25.3; H, 1.3; N, 5.8; Hg, 42.7.

Anal. Calc. for $HgClIC_{10}H_8N_2$: C, 23.1; H, 1.5; N, 5.4; Hg, 38.6; found: C, 23.4; H, 1.9; N, 6.0; Hg, 39.0.

Physical Measurements

Conductivity measurements were carried out at 20 °C in acetonitrile (approx. m*M* concentration) using a WTW conductimeter. The molar conductivities were 139 and 135 mhos cm^2 mol^{-1} for the bromide and iodide respectively. The dipyridyl complexes were insoluble in most common solvents to obtain the molar conductivities.

Molecular weights were determined osmometrically in a Knauer Dampfdruck osmometer in acetonitrile solutions. The molecular weights were 510

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*Author to whom correspondence should be addressed.

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TABLE I. IR and Raman Bands of $(pr_4N)_2Hg_2Cl_4Br_2$.

IR 300 K	IR 77 K	Raman 77 K	Raman Single Crystal	Raman Powder	Raman Solution	Assignment
302 w	304 w	309 w		309 w	305 w (dp?)	ν(Hg–Cl_t)
283 vs	293 vs	283 vs	283 vs	283 vs	279 s (p)	ν(Hg–Cl_t)
226 mw	231 vw	223 ms	224 m	220 m		ν(Hg–Cl_b)
		215 m				ν(Hg–Cl_b)
	208 ms	205 m			208vw (dp?)	ν(Hg–Cl_b)
196 ms	198 m	195 s	194 s	194 s		ν(Hg–Br_t)
165 ms	170 vs		170 mw		184 s(p)	ν(Hg–Br_t)
	123 ms	125 mw	126 mw			bending
113 m	114 w					and
105 m	110 m	90 w	93 w	92 m		lattice
77 ms	79 s	76 w				modes
73 ms	66 m		61 w	61 w		
52 vw	54 vw					

TABLE II. IR and Raman Bands of $(pr_4N)_2Hg_2Cl_4I_2$.

IR 300 K	IR 77 K	Raman 77 K	Raman Single Crystal	Raman Powder	Raman Solution	Assignment
	292 w	307 vw	304 vw	309 vw	308 mw(dp)	ν(Hg–Cl_t)
268 vs	271 vs	268 ms	269 m	273 m	275 s (p)	ν(Hg–Cl_t)
			228 w	222 vw		ν(Hg–Cl_b)
	205 m	215 mw	214 mw			ν(Hg–Cl_b)
175 s,br	182 s,br	192 s	182 w			ν(Hg–Cl_b)
			173 vw			ν(Hg–Cl_b)
156 vs	161 ms	157 ms	159 vs	159 ms	158 m (p)	ν(Hg-I_t)
	158 m	146 vs	156 s	139 vs	140 m (p)	ν(Hg-I_t)
114 vw		122 w		121 w		bending
110 w	112 w			102 vw		and
96 s	95 m					lattice
90 ms			89 w	89 m		modes
80 mw	83 w					
71 mw	79 w		70 vw			
60 m	60 m		66 vw	58 w		
57 m						

(calc. 537.8) for the bromide and 540 (calc. 584.8) for the iodide. To estimate the molecular weights of the solids, the Rast method in camphor was used. The values were 1060 and 1129 for the bromide and iodide respectively.

The far-ir spectra were obtained at room and liquid nitrogen temperatures on a purged Bruker IFS 114 Fourier spectrophotometer using a 5 μ beam splitter at 4 cm^{-1} resolution. The samples were run in polyethylene pellets with 250 scans per sample.

Raman spectra were obtained on a Spex compact 1301 system coupled to a photon-counter and equipped with a He/Ne laser. Solution spectra were obtained from saturated solutions using acetonitrile as solvent.

Results and Discussion

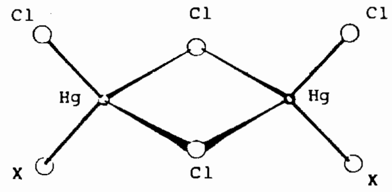
The molecular weight and conductivity measurements in acetonitrile clearly show that the dichlorobromo and dichloroiodomercurate(II) anions as salts of tetrapropylammonium are monomeric and typical 1:1 electrolytes in that solvent. In the solid state, the Rast method indicates that the dimeric species are present and hence the compounds must be formulated as $(Pr_4N)_2Hg_2Cl_4X_2$ (Pr_4N = tetrapropylammonium cation). In addition, the Raman spectra of highly concentrated solutions in acetonitrile show four bands in each case. In both cases, two bands were located at *ca.* 275 and 305 cm^{-1}, bands that can be assigned to the mercury–chloride stretching modes. The remaining bands are detected in the range of 200–180 and 160–140 cm^{-1} in the bromide and iodide respectively. These bands are clearly mercury–bromide or iodide stretching modes.

These results would indicate that in concentrated solutions the dimeric species are also present. Therefore the anionic $Hg_2Cl_4X_2^{=}$ complexes must undergo extensive dissociation on dilution.

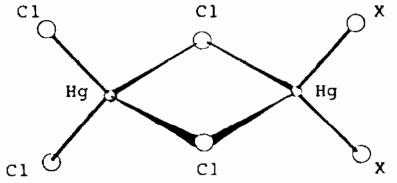
Tables I and II give the IR and Raman bands of the title compounds both in solution and in the solid state. The vibrational spectra are consistent with halogen-bridges and hence the $Hg_2Cl_4X_2^{=}$ anions must possess either D_{2h}, C_{2v}, C_i, C_s or C_1 symmetries. In any case four terminal (T) and four bridging (B) stretching modes are to be observed in the IR and Raman. The bendings, twistings, rockings and deformation modes are observed in a region where the lattice modes also occur and hence we will confine our discussion to the stretching modes frequency region only.

From Tables I and II it can be inferred that a complete coincidence of the IR and Raman bands is observed and therefore the D_{2h} and C_i symmetries can be easily ruled out. The remaining three symmetries imply structures of the type: A, B, C.

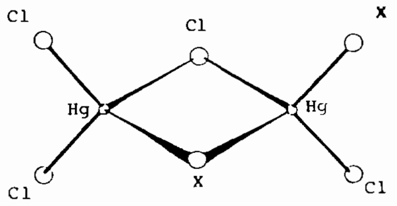
Structures A and B can be easily differentiated from C, since in the former four bridging and two terminal mercury–chloride stretching modes are to be observed in the IR and Raman, whereas only two terminals must be detected for the mercury-bromide or iodide modes. In type C structure, two bridging and three terminal mercury–chloride stretching modes and two bridging and one terminal mercury–bromide or iodide must be observed.



(A)



(B)



(C)

In a mercury–chloride system the stretching modes occur in the range 180–310 cm^{-1}, whereas in the mercury–bromide this range is lowered down to 160–200 cm^{-1} [5, 6, 9]. The mercury–iodide stretching modes are observed between 100–160 cm^{-1} [4, 10]. The dichloroiodomercurate(II) anion shows two bands at *ca.* 270 and 305 cm^{-1} and four bands in the region of 200–175 cm^{-1}. The former are clearly terminal mercury–chloride stretching modes, whereas the latter are bridging modes. This species also shows two medium-to-strong bands in the terminal mercury–iodide stretching frequency region, and hence a structure of the type A or B is the most likely to occur. For the dichlorobromomercurate(II) species the situation is more complex, since both the bridging mercury–chloride and the terminal mercury–bromide frequency regions overlap. However, we have tentatively assigned the bands on the basis of the findings of $Hg_2Cl_6^{=}$ [6] and $Hg_2Br_6^{=}$ [9] and believe that the IR and Raman spectra can be interpreted also on the basis of A or B type structures.

Since vibrational spectroscopy cannot differentiate between A and B type structures, we have carried out some reactions of the title compounds with a well known bridge-breaking ligand such as 2,2′-dipyridyl. If type A structure is present, the main reaction product will be HgClXdipy (X = Br or I) with $HgCl_3X^-$ as side product. On the other hand, if the solids possess a B structure, the main product will be either $HgCl_2$dipy or HgX_2dipy with $HgCl_2X_2^{=}$ or $HgCl_4^{=}$ as side products respectively.

In fact, when reacting the dichlorobromo and dichloriodomercurate(II) species with dipy, the HgClXdipy complexes are obtained (see experi-

TABLE III. Raman Bands (cm^{-1}) of Some Dipyridyl Complexes of the Type HgClXdipy (X = Br or I) and HgX_2dipy (X = Cl, Br or I).

Compound	ν(Hg–N)	ν(Hg–Cl)	ν(Hg–Br)	ν(Hg–I)
HgClBr dipy	258 m	224 m	188 m	
	238 mw			
HgClI dipy	258 mw	221 m		161 vs
	243 w			127 m
$HgCl_2$ dipy	264 m	261 w		
	236 w			
$HgBr_2$ dipy	246 mw		189 s	
			175 m	
HgI_2 dipy	279 w			161 mw
	247 w			142 vs

mental part). Table III shows some characteristic Raman bands of the HgClXdipy and HgX_2dipy complexes and their assignments. The ν(Hg–Cl) modes in the HgClXdipy are rather low as compared with the values observed in $HgCl_2$dipy. This is clearly a halogen-substitution effect. It is worth noting that in no case was the $HgCl_3X^{=}$ species detected, but a mixture of $HgCl_3^-$ and X^-. This result is in keeping with the fact that we have been unable to prepare these mixed four coordinate complexes. In both cases (X = Br or I) the unreacted $HgCl_3^-$ and the corresponding tetrapropylammonium halide have been recovered.

Finally, we believe that the B type structure is unlikely to occur since it would involve the addition of quasi-molecular HgX_2 to the tetrachloromercurate-(II) anion or a complete halogen reordering as the $HgCl_2X^-$ dimerizes.

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