

## THE VIBRATIONAL SPECTRUM OF (BROMOMETHYL)- MERCURY(II) BROMIDE

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### Summary

The preparation and vibrational spectrum of  $\text{BrCH}_2\text{HgBr}$  are reported and a complete vibrational assignment is proposed on the basis of  $C_s$  molecular symmetry. The preparation and a partial vibrational assignment of  $\text{BrCH}_2\text{HgONO}_2$  is also reported.

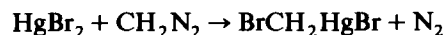
### Introduction

In a spectroscopic study to assess quantitatively the effect of substitution of a halogen atom in the methyl group of  $\text{CH}_3\text{HgCl}$  and  $\text{CH}_3\text{HgONO}_2$  on the Hg–Cl and Hg–O bonds, the infrared and Raman spectra of  $\text{ClCH}_2\text{HgCl}$  [1] and  $\text{ClCH}_2\text{HgONO}_2$  [2] have been reported. It was found that the electronegativity of the chlorine atom in the  $\text{ClCH}_2\text{Hg}$  group aided the bond fission of Hg–O to nitrate ion in aqueous solution. Given the lower electronegativity of bromine than of chlorine it was of interest to consider the effect of the analogous introduction of bromine into the  $\text{CH}_3\text{Hg}$  group.

### Experimental

#### *Preparation of $\text{BrCH}_2\text{HgBr}$*

Bromomethylmercury (II) bromide was prepared as described by Hellerman and Newman [3] but with modifications similar to those described for the preparation of  $\text{ClCH}_2\text{HgCl}$  [1]. The method involved the distillation of ethereal diazomethane into a suspension of excess mercury(II) bromide in ether, to give the following reaction:



[Use of an excess of diazomethane would result in further reaction to form the bis-compound,  $(\text{CH}_2\text{Br})_2\text{Hg}$ ]. Experimental details have been given previously [1]; during the reaction the bromomethylmercury(II) bromide separates from the ethereal solution. For the work-up solvent was evaporated and the crude product twice

TABLE 1

FREQUENCIES AND ASSIGNMENTS IN THE VIBRATIONAL SPECTRUM OF  $\text{BrCH}_2\text{HgBr}$ 

Raman		Infra-red	Symmetry	Assignment
Solution	Solid	Solid	class	
0.2 M in MeCN				
–	96w	90m	A''	C–Hg–Br deformation
130mw,	132m	126ms	A'	C–Hg–Br deformation
232vs, pol.	215vs	221s	A'	Hg–Br stretch
486m, pol.	483m	479m	A'	Hg–C stretch
510s, pol.	514s	510m	A'	C–Br stretch
633ms, pol.	637m	634s	A'	$\text{CH}_2\text{Br}$ rock
691m, depol.	693m	687s	A''	$\text{CH}_2\text{Br}$ rock
1044s, depol	1048m	1045m	A'	$\text{CH}_2$ deformation
1122m, pol.	1120m	1120s	A''	CHBr deformation
1221ms, pol.	1225m	1220s	A'	$\text{CH}_2$ deformation
n.o. <sup>a</sup>	2948m	2954ms	A'	CH symmetric stretch
n.o. <sup>a</sup>	3020m	3025s	A''	CH asymmetric stretch

<sup>a</sup> n.o. = not observed.

recrystallised from anhydrous methanol to give white leaflets of  $\text{BrCH}_2\text{HgBr}$ . The yield was approximately 60%. The solid was analysed for mercury by Kharasch and Flenner's method [4] and for bromine by reaction with sodium in methanol followed by precipitation as  $\text{AgBr}$ . The results were as follows: Found: Hg, 53.86; Br, 42.39;  $\text{BrCH}_2\text{HgBr}$  calcd.: Hg, 53.57; Br, 42.68%.

The results confirmed that the recrystallised sample was pure  $\text{BrCH}_2\text{HgBr}$ .

### Spectra

Raman spectra were obtained from solid bromomethylmercury(II) bromide and from 0.2 M solution in methyl cyanide. Spectra were excited with the 514.5 nm line of an argon-ion laser (power 500 mW at the sample) and recorded with a Spex Instruments 1401 double monochromator with photon-counting detection. It was necessary to cool the solutions to  $\sim 5^\circ\text{C}$  with a jacketted cell and cool air to minimise the photolytic decomposition of the samples. The solid sample was stable in the laser beam at ambient temperatures. The Raman spectra were calibrated by use of neon emission lines, and vibrational wavenumbers are accurate to  $\pm 2\text{ cm}^{-1}$ .

Infrared spectra were recorded with Nujol mulls using Perkin–Elmer 521 ( $4000\text{--}400\text{ cm}^{-1}$  range) and Beckmann IR11 ( $800\text{--}33\text{ cm}^{-1}$  range) spectrometers. Calibration was effected using polythene and indene spectra and the vibrational wavenumbers are accurate to  $\pm 1\text{ cm}^{-1}$ .

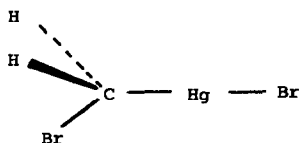


Fig. 1. The molecular structure of  $\text{BrCH}_2\text{HgBr}$ .

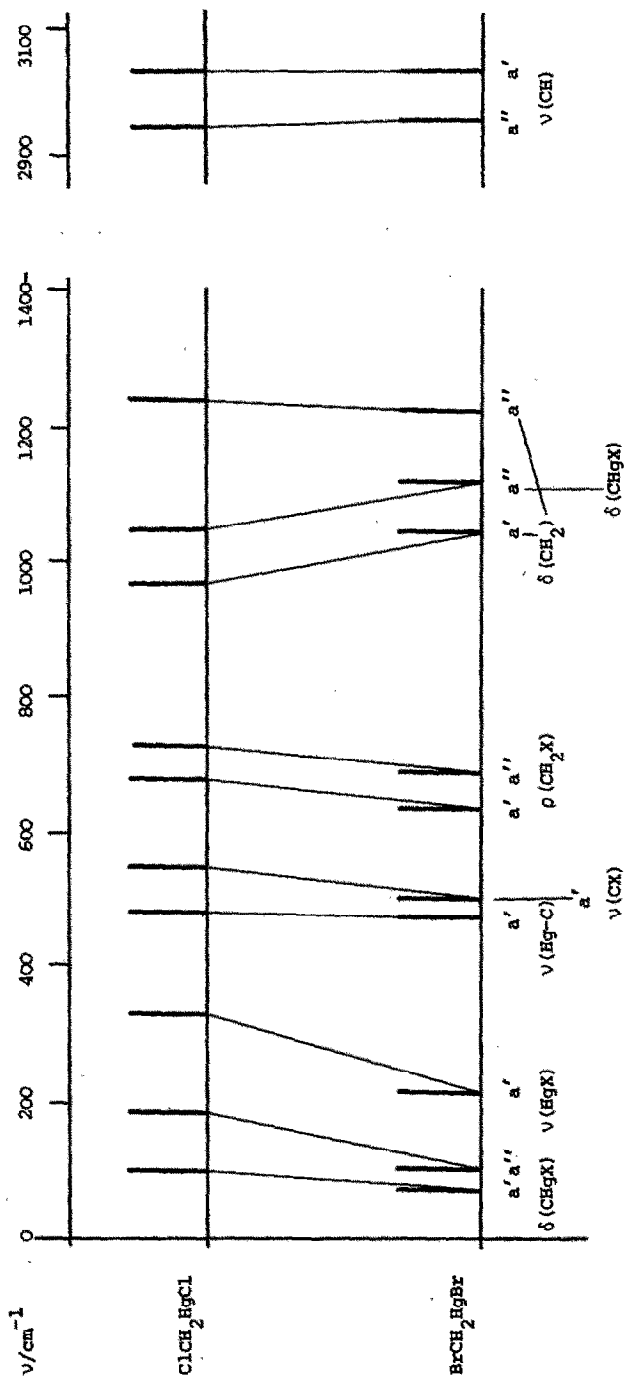


Fig. 2. Vibrational spectra and correlation diagram for  $\text{XCH}_2\text{HgX}$  where  $\text{X} = \text{Br}$  and  $\text{Cl}$ .

### Assignment of spectra

The wavenumbers from the Raman and infrared spectra, their assignments and the approximate descriptions of the vibrational modes are shown in Table 1. The structure of the molecule, shown in Fig. 1, has  $C_s$  symmetry for which  $\Gamma_{\text{vib}} = 8A' + 4A''$ .

All these vibrational modes are active in both Raman and infrared spectra, and eight polarised bands are to be expected in the Raman spectra of solutions of  $\text{BrCH}_2\text{HgBr}$ .

Six polarised bands were identified in the Raman spectrum of a methyl cyanide solution of bromomethylmercury(II) bromide; two other bands, observed in the solid in the  $\nu(\text{C-H})$  stretching region, are not observed in the solution because of interference from the solvent, and one feature at  $\Delta\tilde{\nu} 130 \text{ cm}^{-1}$  is too weak for its depolarisation ratio to be determined. The assignment of the  $A'$  and  $A''$  species vibrations follows from comparison with the spectra of  $\text{CH}_3\text{HgCl}$  [5] and  $\text{ClCH}_2\text{HgCl}$  [1].

The strong polarised band in the Raman spectrum at  $\Delta\tilde{\nu} 232 \text{ cm}^{-1}$  ( $215 \text{ cm}^{-1}$  in the solid) has a counterpart at  $221 \text{ cm}^{-1}$  in the infrared spectrum of the solid, and is assigned to the  $\nu(\text{Hg-Br})$  stretching vibration. The  $\nu(\text{Hg-C})$  stretching frequency,  $483$  and  $479 \text{ cm}^{-1}$  in the Raman and infra-red spectra, respectively, is comparable with that for the similar vibration at  $570 \text{ cm}^{-1}$  in  $\text{CH}_3\text{HgCl}$  and  $486 \text{ cm}^{-1}$  in  $\text{ClCH}_2\text{HgCl}$ . The other strong, polarised band in this region at  $510 \text{ cm}^{-1}$  in the infrared and at  $510 \text{ cm}^{-1}$  in the Raman spectrum of the solution can be assigned to the  $\nu(\text{C-Br})$  stretching vibration. The assignment of the other  $A'$  and  $A''$  modes based on the  $\text{CH}_2$  group vibrations follows by analogy with the other organomercury halides.

Figure 2 shows a correlation diagram for the vibrational spectra of  $\text{BrCH}_2\text{HgBr}$  and  $\text{ClCH}_2\text{HgCl}$  [1]. The correlation for the bromo and chloro species is extremely good, and lends support to the assignment in Table 1 for the  $\text{BrCH}_2\text{HgBr}$  species.

The frequency of  $\nu(\text{Hg-X})$ , (where  $X = \text{Cl, Br}$ ) is not changed at all on going from the  $\text{XCH}_2\text{HgX}$  species to the  $\text{HgX}_2$  species, although the  $\nu(\text{Hg-C})$  frequency is different from that for  $\text{CH}_3\text{HgX}$ . At first sight the similarity of the  $\nu(\text{Hg-X})$  in a series of molecules following introduction of  $X$  into the methyl group of  $\text{CH}_3\text{HgX}$  is surprising. This is especially so when one considers the related molecules  $\text{CH}_3\text{HgONO}_2$  and  $\text{ClCH}_2\text{HgONO}_2$ , in which the introduction of  $\text{Cl}$  into the methyl group produces a 100-fold increase in the dissociation of the  $\text{ONO}_2$  group. It was also noted recently [1] that the effect of introduction of a chlorine atom in the methyl group of  $\text{CH}_3\text{HgCl}$  was not transmitted to the  $\text{Hg-Cl}$  bond. Quantitative comparison of introduction of  $\text{Br}$  and  $\text{Cl}$  substituents into  $\text{CH}_3\text{HgCl}$  must await the results of force constant calculations on  $\text{BrCH}_2\text{HgBr}$ .

### Preparation of bromomethylmercury(II) nitrate

Samples of bromomethylmercury(II) nitrate were made by mixing stoichiometric quantities of bromomethylmercury(II) bromide and silver nitrate in warm methyl cyanide. Silver bromide was filtered off and the methyl cyanide removed from the filtrate under vacuum at room temperature. Since silver bromide is itself somewhat soluble in methyl cyanide, the solid remaining after removal of the methyl cyanide in the filtrate was extracted with cold water. Vacuum dessication of the aqueous

extracts over phosphorus(V) oxide gave pure white leaflets (Found: Hg, 56.34; NO<sub>3</sub>, 17.17; Br, 22.60; BrCH<sub>2</sub>HgONO<sub>2</sub> calcd.: Hg, 56.26; NO<sub>3</sub>, 17.39; Br, 22.41%).

A partial characterisation of the BrCH<sub>2</sub>HgONO<sub>2</sub> molecule was obtained from a study of the infra-red spectrum of the solid; Nujol mulls were used, and spectra were recorded with Perkin-Elmer 521 (3000–650 cm<sup>-1</sup>) and Beckman IR11 (800–33 cm<sup>-1</sup>) spectrometers. Bands were observed at 640 (a'', NO<sub>2</sub> deformation), 1030 (a', N–O stretch, Hg–O bonded), 1340 (broad, a', NO<sub>2</sub> stretch) and 1460 cm<sup>-1</sup> (broad, a'', NO<sub>2</sub> stretch) in addition to bands attributable to the BrCH<sub>2</sub>Hg entity. The spectrum indicates that the nitrate is coordinated in monodentate fashion to mercury. In the Raman spectrum of an aqueous solution of BrCH<sub>2</sub>HgONO<sub>2</sub> (saturated, 0.05 M, at 5°C) excited by 488.0 nm laser radiation only a weak feature at  $\Delta\tilde{\nu}$  1049 cm<sup>-1</sup> could be identified, and this indicates that some or all nitrate exists as NO<sub>3</sub><sup>-</sup>. Since stronger aqueous solutions could not be obtained it was impossible to establish quantitatively the effect of introduction of Br into CH<sub>3</sub>HgONO<sub>2</sub> on the dissociation of the nitrate in aqueous solution. The fall in solubility in aqueous solution of XCH<sub>2</sub>HgONO<sub>2</sub> compounds on going from X = H to Cl, and Br is marked; thus saturated aqueous solutions contain 7, 0.08 and 0.005 mol l<sup>-1</sup> for X = H, Cl, and Br, respectively. Although the solubility of BrCH<sub>2</sub>HgONO<sub>2</sub> is greater in methyl cyanide, these solutions are too unstable for Raman spectroscopic work, and so complete vibrational assignment of BrCH<sub>2</sub>HgONO<sub>2</sub> was not possible.

## References

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