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# The Structure of Methylmercury(II) Hydroxide in Aqueous Solution

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## Abstract

The structure of $CH_3HgOH$ in an aqueous solution of pH = 9 was determined by an X-ray scattering technique at 25 °C. Linear methylmercury(II) hydroxide species is confirmed to predominate, and no polynuclear complexes are found. The 2.06(2) Å (Hg–O) and 2.04(3) Å (Hg–C) distances in the methylmercury(II) complex can not be significantly separated from each other. These bond distances are in good agreement with those found in the gaseous and solid phases in related compounds. Water is totally absent from the inner coordination sphere of mercury. The solvation occurs through hydrogen bondings to the hydroxide group and through van der Waals forces to the molecule. Distribution equilibria between air and water, Henry's law constants, for methylmercury(II) complexes are compared with the derived structural information on the solvated complexes. Raman spectroscopy has been used qualitatively to identify methylmercury(II) hydroxide in the experimental solution prior to the scattering study.

## Introduction

Large angle X-ray scattering (LAXS) is a useful technique for structural examination of the coordination chemistry of methylmercury(II) in solution. A direct investigation of the dissolved mercury species is possible if the solubility is sufficiently high. The coordination chemistry of solvated methylmercury(II) complexes may be accurately resolved by combining data from X-ray diffraction and spectroscopic methods (*e.g.* Raman and NMR) [1–7], together with complex formation constants [4, 8].

Several important physical and chemical properties of methylmercury(II) complexes are closely related to the coordination chemistry in aqueous solution. For example, the hydration has a direct effect on the solubility of the complexes. Also, distribution equilibria for methylmercury(II) species between water and various other phases (*e.g.* gas and organic phases) are very important parameters in explaining transport phenomena. Henry's law constant ($H$) expresses thermodynamically the transport direction between air and water if the concentrations in both phases are known [9, 10]. The magnitude of $H$ is dependent on interactions between the solvent and the methylmercury(II) compound including the ligand. Both the coordination strength and the entropy effect must, however, be considered.

Methylmercury(II) was recognized as a very important environmental form of mercury after the poisoning of inhabitants in Minamata, Japan, in the 1950s [11]. Methylmercury(II) is the main mercury species found in fish and mammals, although it is considered to be a very small fraction of the total mercury in the atmosphere and in natural waters [10]. There is a need for accurate data concerning the complexation and interaction with water, as well as the kinetics of formation/destruction of methylmercury(II) compounds. Structural information regarding methylmercury(II) complexes in aqueous solution may contribute to resolving accumulation pathways in natural systems.

The structural determination of $CH_3HgOH$ performed in the present investigation is the first in a series of structural examinations of methylmercury(II) complexes in various solvents. Methylmercury(II) compounds have pronounced linear two-coordination [4, 12]. It was therefore of interest to confirm the very weak interactions expected between these species and water. The study of methylmercury(II) hydroxide was further intended to contribute to resolving the dispute regarding the existence of the complex in aqueous solution [4]. The Schwarzenbach/Schellenberg acid–base model [8], supported by Raman and NMR spectral data [1–3, 6, 13], predicts methylmercury(II) hydroxide as the main species at high pH. This has been confirmed in the present study. It was also of interest to examine the effect of the soft methyl ligand on the solvated

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mercury structures [14–18]. The strength of solvation is shown by comparing Henry's law constants for inorganic mercury(II) and methylmercury(II) species [19]. Finally, Raman spectroscopy is applied to identify methylmercury(II) hydroxide as the predominant species in the aqueous solution used in the structural determination.

## Experimental

### *Chemicals*

A commercial 1 M aqueous solution of methylmercury(II) hydroxide (Ventron) was used in the scattering experiment. A pH of 9.45 resulted in a negligible amount of dissolved inorganic mercury complexes, due to the low solubility of HgO(s) [20].

### *Analysis*

The methylmercury(II) hydroxide concentration of the commercial solution was found to be 1.15 M. Volatilization of mercury from diluted samples after treatment with $NaBH_4$ was used as analysis technique [9]. Mercury from the samples was preconcentrated on gold traps. The gold traps were subsequently analyzed and calibrated using a helium d.c. plasma emission spectrometer [9, 21].

### *X-ray Scattering Measurement*

The scattering study was performed using a large angle $\theta-\theta$ diffractometer to measure scattering X-ray intensities from the surface of the solution [17, 22, 23]. The experimental solution was enclosed in a cylindrical thin-walled glass container [24] in order to avoid any hazardous contact during the diffraction experiment. The glass container, exactly half-filled with solution, was mounted inside the air-tight sample housing. Mo K$\alpha$, $\lambda = 0.7107$ Å, was used in the experiment. The angle dependence in absorption of the glass container was calibrated in the same way as previously described [24]. The correction factor, derived from the intensity ratio between open-cup and glass-container measurements of 0.5 M $Hg_2I^{3+}$ in dimethylsulfoxide, was idealized to smooth line. All data below $\theta = 5°$ were extrapolated depending on the upward meniscus [24]. The X-ray beam passed through a LiF monochromator after scattering but before reaching the scintillation detector. The scattered intensity was measured at discrete points, at intervals of 0.1° in the range $5° < \theta < 30°$, and at intervals of 0.25° in the range $30° < \theta < 63°$. 40 000 counts at each sampling point were collected over a scattering angle ($2\theta$) of 10° to 126°. All measurements were repeated twice, corresponding to an error in counting statistics of 0.35%. Small irregularities in the glass wall were considered to be responsible for the somewhat higher spread between data points than normally found. The incoherent scattering reaching the counter after passage of the monochromator was investigated according to a standard procedure [14]. The scattering experiment was performed at 25 ± 1 °C.

### *Data Treatment*

Measured intensity data were initially corrected for background and polarization [22]. Normalization of corrected intensity data to a stoichiometric unit of volume, $V$, corresponding to the solution volume containing one Hg atom, was performed. The normalization factor was derived from comparison of measured and total independent theoretical scattering in the high angle region, $s > 13.5$ Å$^{-1}$, where $s = 4\pi \sin\theta/\lambda$. The normalization factor was in good agreement with a factor calculated by a standard integration method [25, 26].

Scattering factors, $f$, for neutral atoms [27] were used, with the exception that spherical form factors were chosen for H and $H_2O$ [28, 29]. The contribution from anomalous dispersion, $\Delta f'$ and $\Delta f''$, was considered for all atoms [27]. Incoherent scattering factors [30–32] corrected for the Breit–Dirac effect [33, 34] were used. The function *del*($s$), which estimated the fraction of incoherent radiation passing the monochromator, was also applied in the correction for incoherent radiation [14].

The reduced intensity, $i(s)$, was calculated from corrected and scaled intensity data, $I_{obs}(s)$ according to

$$i(s) = I_{obs}(s) - \sum_m [(f_m(s) + \Delta f'_m)^2 + (\Delta f''_m)^2]$$

The differential electronic radial distribution function, RDF, was consequently derived from the intensity function $i(s)$ by a Fourier transformation.

$$D(r) - 4\pi r^2 \rho_0 = (2r/\pi)\int_0^{s_{max}} s i(s) M(s) \sin(rs) ds$$

where

$$\rho_0 = \left\{\left[\sum_m (f_m + \Delta f'_m)\right]^2 + \left(\sum_m \Delta f''_m\right)^2\right\} \Big/ V$$

and

$$M(s) = [f_{Hg}{}^2(0)/f_{Hg}{}^2(s)] \exp(-0.01 s^2)$$

$M(s)$ denotes a modification function, fully described elsewhere [24]. A standard procedure involving Fourier transformation was applied to remove spurious peaks below 1.5 Å in the RDF [22]. The calculated reduced intensities from the assigned interatomic interactions in models [35] were treated in the same way as the experimental reduced intensity function. Completely comparable model functions were, subsequently, derived from the Fourier transformation. All calculations were made using the program KURVLR [35].

Least-squares refinements of the main interactions in the models were performed using the reduced intensities $i_{obs}(s)$ and $i_{calc}(s)$, minimizing

$$U = \sum_{s_{min}}^{s_{max}} w(s)[i_{obs}(s) - i_{calc}(s)]^2$$

by means of the PUTSLR [35] and STEPLR programs [36]. Here $w(s)$ denotes a weighting function proportional to $I_{obs}^{-2} \cos \theta$. The remaining distances, temperature factor coefficients and frequencies have been revealed from the RDF values. These parameters can not be refined because contributions of the interactions to the intensity function are too small. Instead, these parameters have been systematically varied in order to obtain an optimum fit in the RDF.

### *Raman Measurements*

Raman spectra were recorded on a CARY 82 argon-ion laser spectrometer using the 4880 Å line. Spectra were obtained throughout the range 100–1,000 cm$^{-1}$ from samples stored in glass tubes ($\phi$ 1 mm).

## Results and Discussion

The pH dependence of methylmercury(II) hydroxide in pure aqueous solution have been described by the following reactions [4, 6, 8], with $K_1$ and $K_2$ quoted from Ref. 8:

$$CH_3HgOH_2^+ + OH^- \rightleftarrows CH_3HgOH + H_2O \quad K_1 = 10^{9.37}$$

$$CH_3HgOH_2^+ + CH_3HgOH \rightleftarrows (CH_3Hg)_2OH^+ + H_2O \quad K_2 = 10^{2.37}$$

Of less importance is the proposed additional reaction occurring to a very minor extent at neutral pH [4, 6].

$$CH_3HgOH + (CH_3Hg)_2OH^+ \rightleftarrows (CH_3Hg)_3O^+ + H_2O \quad K_3 \approx 0.3–0.7$$

Methylmercury(II) hydroxide was expected, from the equations above, to be strongly predominant (99%) at the pH used in the present investigation. However, previous investigations did not confirm the existence of the mononuclear methylmercury(II) hydroxide complex and suggested that the interpretation of the Raman spectral data for an aqueous solution of this species was incorrect [1, 37]. Instead, the occurrence of a predominating polynuclear compound was suggested. Other studies presented both Raman and NMR data which strongly indicated the objection to be without convincing support [1, 4, 6]. The Raman stretching vibrations, $\nu$(Hg–O) and $\nu$(Hg–C), were found to be 504 cm$^{-1}$ and 570 cm$^{-1}$, respectively, for the solution used in the present X-ray scattering study. The corresponding stretching vibrations found were 505 and 569 cm$^{-1}$ for a 0.050 M aqueous solution [7], 504 and around 570 cm$^{-1}$ for a 0.510 M methylmercury(II) hydroxide aqueous solution [6] and 511 and 577 cm$^{-1}$ for a 4 M solution [1]. The structural determination was thus performed on a solution in which methylmercury(II) hydroxide was ascribed to be the strongly predominant species.

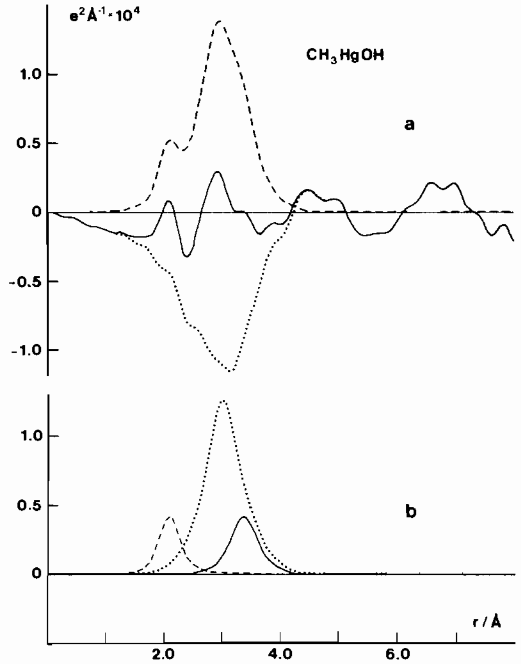

Fig. 1. (a) Experimental differential radial distribution function, $D(r) - 4\pi r^2 \rho_0$, for methylmercury(II) hydroxide in aqueous solution (solid line), the sum of theoretical interactions (dashed line) and the calculated difference between the two RDF's (dotten line). (b) Calculated specific interactions and their contribution to the RDF model function: sum of Hg–$CH_3$ and Hg–OH interactions (dashed line), free water structure (dotted line), Hg–water interaction, where the water is found at the approximate sum of van der Waals radii (solid line).

The differential radial distribution function, RDF $= D(r) - 4\pi r^2 \rho_0$, shows several significant peaks (Fig. 1). The peak at 2.1 Å consists of two different bond distances in methylmercury(II) hydroxide, Hg–O and Hg–C, which are not distinguishably separated from each other. Corresponding structural data on gaseous or solid methylmercury(II) hydroxide, of which the latter has not yet been possible to synthesize [37, 38], are not resolved. As a firm basis for interpretation of the solvated structure, comparable distances were taken from various compounds exhibiting two-coordinated mercury. The

Hg–O distances in some crystal structures with linear or near-linear two-coordinated mercury (167.7–180°) were found in the range 2.028–2.099 Å [39–42]. Gas phase structures of $CH_3HgX$ (X = Cl, Br and I) [43] and $CH_3HgCH_3$ [44] revealed Hg–C bond lengths between 2.052 and 2.080 Å. Thus the Hg–O and Hg–C distances in solvated methylmercury(II) hydroxide in water seem to be reasonable. The bulk structure, *i.e.* the water–water interactions within the free water, generates the RDF peak typical for aqueous solutions at 2.9 Å [45], see Fig. 1b.

The total absence of mercury–solvent interactions, beside van der Waals forces, is strongly indicated by the shoulder at 3.3 Å. This peak is assumed to be at the sum of van der Waals radii. The reported van der Waals radius for Hg varies between 1.5 Å and 1.73 Å [12, 46]. The oxygen van der Waals radius in water has not been reported. On the other hand, the ionic radius of two- and three-coordinated oxygen at 1.35 Å and 1.36 Å [47], respectively, has been applied to calculate the octahedral ionic radius of $Hg^{2+}$ in water and dimethylsulfoxide [14]. A larger oxygen van der Waals radius thus seems possible when compared to the ionic radius. The maximum value of the mercury radius is applied. The determined sum of van der Waals radii for mercury–oxygen(water) give a minimum oxygen van der Waals radius of 1.57 Å. This value may be compared to the value 1.40 Å [48], frequently used in solid structures. No peak corresponding to a closer coordination of water molecules can be found. If the water molecules at 3.3 Å are regarded as perpendicularly oriented towards the C–Hg–O axis, the peak at 3.8 Å may be explained as C–O(water) and O–O(water) interactions. The 3.3 Å distance is thus regarded as the closest one a water molecule may approach the mercury in methylmercury(II) hydroxide during an average period of time. These peaks are absent in the RDF found for the regular octahedron of solvated inorganic mercury(II) in water [14].

The fact that water can not be found in the inner coordination sphere of mercury in methylmercury(II) hydroxide is further evidenced by the smooth RDF, with no apparent asymmetry in the interval 2.4 to 2.9 Å where such a bond length would be expected. The range is derived from a number of Hg–O distances in solution and crystals. The Hg–O bond distance in the hydrated mercury(II) ion, $Hg(H_2O)_6^{2+}$, is 2.41 Å [14], while the corresponding regularly octahedral dimethylsulfoxide solvate exhibits a Hg–O distance of 2.39 Å in dimethylsulfoxide solution [14]. The uncharged complexes $HgX_2$ (X = Cl, Br and I) and $Hg(SCN)_2$ in dimethylsulfoxide [15, 18], as well as mercury(II) chloride in methanol [18], coordinate solvent molecules via oxygen. The Hg–O bond distances are in the range 2.6–2.7 Å. Weak Hg–O interactions, nitrate or carboxylate group, at distances around 2.8–2.9 Å, have been revealed from crystal structures of methylmercury(II) compounds with nitrogen-donating ligands [49–52].

The difference between the experimental and the calculated differential RDF, including the water structure and the Hg–O and Hg–C distances, is also informative. A diffuse shoulder is displayed at 2.6 Å. A peak arising from the hydrogen bonding between hydroxide and water is expected to be found at this distance. The hydroxide group of methylmercury(II) hydroxide is able to form hydrogen bonds with water, even in the absence of water in the inner coordination sphere of mercury. This is most probably one reason for the considerably larger solubility of methylmercury(II) hydroxide in water compared to the methylmercury(II) halides. It should be stressed that the shoulder is far too small to reflect any mercury–water interaction, which has been tested by model calculations (*cf.* refinements on the reduced intensities). The occurrence of the two peaks, 3.3 Å and 3.8 Å, supports the presence of a completely linear methylmercury(II) hydroxide molecule in water with no mercury–water interaction in the first coordination sphere. This can be stated in spite of the fact that a direct investigation of the linearity is impossible. The relatively small contribution from the C–O distance to the intensity function is the reason why the C–Hg–O angle can not be observed by this technique.

The difference in Henry's law constant, *H*, for some methylmercury(II) compounds can now be supported from a structural basis (see Table I). The variation in *H* is obviously not due to varying strength in the solvating interaction between mercury and the aqueous solvent, *cf.* assessed linear complexes. Instead, solvation of the ligand appears to be important when considering the pronounced variation in *H*.

From these results it seems possible to forecast a trend in *H* for methylmercury(II) species in general. Henry's law constants in Table I may also be compared to *H* at 25 °C for elemental mercury, 0.29 (dimensionless) [53]. This further indicates that the magnitude of *H* will be in the same order only if solvation occurs through van der Waals forces of the same strength and if the entropy of solvation is similar.

The broad peaks between 4 and 5 Å consist of several interactions (see Fig. 1). The interactions contributing in this range are not discussed, since they are not included in the refined models of solvated methylmercury(II) hydroxide. Contributions to this range arise, however, from the second neighbor water–water interaction in the bulk [45] and several interactions in connection with the second water coordination sphere.

TABLE I. Comparison Between the Solvated Structure of Various Methylmercury(II) Complcxes and the Dimensionless Henry's Law Constant ($H = [CH_3HgX_{(g)}][CH_3HgX_{(aq)}]^{-1}$) at 25 °C

| Species | $H$ | Bond length | | | | C–Hg–X angle in water[a] (°) | Hydrogen bondings |
|---|---|---|---|---|---|---|---|
| | | Gas | | Water | | | |
| | | Hg–C (Å) | Hg–X (Å) | Hg–C (Å) | Hg–X (Å) | | |
| $CH_3HgOH$ | $2.5 \times 10^{-7}$[b] | | | 2.04[c] | 2.06[c] | ~180 | Yes |
| $CH_3HgCl$ | $1.9 \times 10^{-5}$[d] | 2.055[e] | 2.283[e] | 2.07[f] | 2.325[f] | ~180 | Yes |
| $CH_3HgCH_3$ | 0.31[g] | 2.080[h] | | | | ~180 | No |

[a] Angle assessed from Raman stretching frequencies, ref. 54 and refs. therein. [b] Data from ref. 19; determined in $2 \times 10^{-4}$ M NaCl with pH adjusted by NaOH to 11.5. [c] Data from present work. [d] Data from ref. 9; 0.7 M and 1.0 M Na, H(Cl) media. [e] Data from ref. 43. [f] Data from ref. 54. The solvated structure was determined in pyridine. The bond distances in water may be interpreted to be in the interval between gas phase and pyridine data. No refinement of the Hg–C distances could be performed due to overlap from the much stronger Hg–Cl interaction. [g] Data from ref. 55; pure water. [h] Data from ref. 44.

The radial distribution function above 5 Å is not considered because of the large number of uninterpretable long range interactions. These are also most affected by the low $s$ values. The low $s$ interval is strongly influenced by the extrapolation of data below $\theta = 5°$.

The existence of the mono-nuclear methylmercury(II) hydroxide molecule in aqueous solution is evidenced by the assignment of the peaks in the RDF. Further, and most convincingly, a mercury–mercury interaction arising from complex molecules like $(CH_3Hg)_2OH^+$ and $(CH_3Hg)_3O^+$ would have given a large contribution to the RDF. In conclusion, no polynuclear complexes are found in the experimental solution where methylmercury(II) hydroxide is predominant, consistent with reported stability constant data [4, 6, 8].

Least-squares refinements of the Hg–O and Hg–C bond distances were obtained from the reduced intensities in the interval $4.0 < s < 15.8$ Å$^{-1}$. Variation of the lower $s$ limit between 3.5 and 6.0 Å$^{-1}$ gave no deviation in distances. A significant separation of the two interactions was, however, not possible (Table II). The close agreement between the bond lengths resulted in an enlargement of the standard deviation and minimized the possibility of refining accurate temperature coefficients.

A very simple model applied in the beginning included only the Hg–O and Hg–C interactions within the linear methylmercury(II) hydroxide complex and the bulk water structure. A nice fit between the model and experimental data was obtained and the reduced intensity curve was satisfactorily explained down to about 4 Å$^{-1}$. Applying the extended model which included water at the sum of van der Waals radii (see Table II) improved the fit considerably, down to about 3 Å$^{-1}$ (see Fig. 2). No variation in the refined Hg–C and Hg–O distances were seen between the models.

TABLE II. Parameters Applied, and Result of Least-squares Refinements of Interactions, within the Model of $CH_3HgOH$ in Aqueous Solution[a]

| Interaction | Parameter | |
|---|---|---|
| $Hg–CH_3$ | $d$ | 2.04(3) |
| | $b$ | 0.002 |
| | $n$ | 1.0 |
| Hg–OH | $d$ | 2.06(2) |
| | $b$ | 0.002 |
| | $n$ | 1.0 |
| $Hg–H_2O$[b] | $d$ | 3.30 |
| | $b$ | 0.008 |
| | $n$ | 2.0 |
| $H_2O–H_2O$ | $d$ | 2.88 |
| | $b$ | 0.010 |
| | $n$ | 1.67 |

[a] Refinements in the range $5.0 \leqslant s \leqslant 15.8$ of the reduced intensity curve. The refined parameters are given with standard deviations in parentheses. The distance in Å is denoted by $d$; the temperature coefficient, $b$, is given in Å$^2$ and the number of distances per mercury atom is given by $n$. [b] Water found at the approximate sum of van der Waals radii.

The absence of an inner sphere mercury–water interaction was confirmed by refining a model including coordinated water at a distance of 2.6 Å. The theoretical reduced intensity curve was completely out of phase with the experimental data at 7 Å$^{-1}$. Also, the fit at higher $s$ values was worse than that for the simple linear methylmercury(II) hydroxide model without mercury–water interactions, apart from van der Waals forces and hydrogen bonding to the hydroxide.

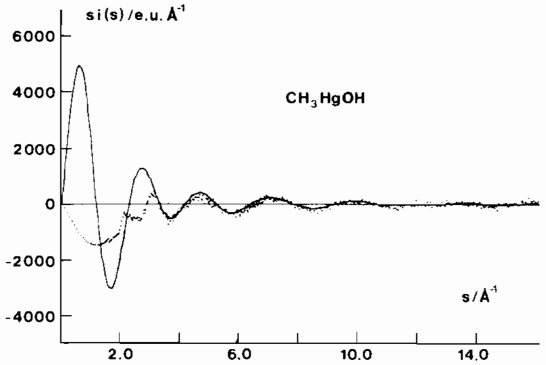

Fig. 2. Experimental *si*(*s*) values (dots) and values calculated from model (solid line). The parameters used in the model are given in Table II.

## Conclusion

Strong evidence for a linear methylmercury(II) hydroxide complex in aqueous solution has been revealed by X-ray scattering. No interaction between mercury and water in the inner coordination sphere exists and methylmercury(II) hydroxide is consequently solvated only by hydrogen bonding to the hydroxide and by van der Waals forces. The closest distance between mercury and water in the second coordination shell is about 3.3 Å, which is in close agreement with the sum of van der Waals radii. The soft methyl group coordinated to mercury probably prevents the occurrence of solvation of mercury in aqueous solution.

The results of the present study and the distribution between air and water (Henry's law constant, *H*) for dimethylmercury and methylmercury(II) chloride indicate that the methylmercury(II) compounds are primarily solvated through the ligand.

The methylmercury(II) hydroxide complex predominates in alkaline aqueous solution. Polynuclear complexes of methylmercury(II) do not exist at the 1.15 M methylmercury(II) hydroxide concentration.

The bond distances Hg–O and Hg–C in methylmercury(II) hydroxide are 2.06(2) and 2.04(3) Å, respectively. The two different bond distances could not be completely separated. The distances are, however, not significantly longer than distances found within different mercury crystal and gas phase structures.

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