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Raman spectroscopic study of the complexation of the methylmercury(II) cation, CH_3Hg^+, by ligands containing oxygen and sulphur

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Abstract

The vibrational Raman spectra of methylmercury(II) nitrate in aqueous solution and of its complexes with dimethyl sulphide and dimethyl sulphoxide (DMSO) are presented. A quantitative determination of the ν(HgO) and ν(HgS) stretching band intensities using the ν(HgC) stretching band as an internal standard for the $CH_3HgOH_2{}^+$ and $CH_3HgS(CH_3)_2{}^+$ species in aqueous solution has shown that the methylmercury(II) dimethyl sulphide complex cation is only partially dissociated in 0.01 *M* aqueous solution, with $\alpha = 0.40$. An estimate of a factor of 2600 for the preference for sulphur coordination to oxygen coordination under these conditions has been made. The dimethyl sulphoxide complex of the methylmercury(II) cation has a mercury–oxygen bond and not mercury–sulphur as expected.

1. Introduction

The methylmercury(II) cation, CH_3Hg^+, is of interest in that it is a bridge between the classical organometallic chemistry of the element and its typical inorganic chemistry. The organometallic cation behaves as a simple inorganic ion in the binding of ligands; the complexes which are formed involve the highly covalent, kinetically inert Hg–C bond together with highly polar bonds from Hg to other ligands. The methylmercury(II) cation has a very strong preference [1] for a coordination number of one and only in the presence of a high concentration of ligands such as I^- or CNS^- does the ion submit to further coordination [2]. Because of this preference, allied with the chemical inertness of the methyl group, the coordination chemistry of CH_3Hg^+ is very simple compared with that of Hg^{2+}.

Like the parent Hg^{2+}, the CH_3Hg^+ ion displays a class B stability order in its complexes [3], and the most stable complexes are those formed with weakly electronegative and highly polarizable ligand atoms [4], especially those complexes involving ion–dipole bonds between mercury and the ligand. In addition, the mercury atom is not electropositive enough for rapid hydrolysis of the Hg–C bond to occur in solution, nor is it electronegative enough for the formation of an organometallic oxide.

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Kraus and Callis [5] have established that the stabilization of an organometallic cation in solution required the solvent to have a high dielectric constant and also to be a good electron donor [6]. The donor properties of the ligand and the stability of the resulting complexes may be explained by the increased shielding effect of the nuclear charge on the mercury atom arising from the low electronegativity of the CH_3 group. Also, greater ease of $5d$–$6s$ mixing and a high $6s$–$6p$ energy separation results in preferred digonal *sp* hybridization for the CH_3Hg^+ species.

Interest in the toxicological properties of organomercurials has centred on their reactivity and transmission through the vital organs of fish and animals [9,10]. The stability of the CH_3Hg^+ species and its mobility in natural food chains to the detriment of the organisms involved has assisted in a bioaccumulation effect with consequent magnification of the toxicity [11,12]. The decomposition of organomercurials has been studied under laboratory conditions and it has been found [13] that the CH_3Hg^+ species has a half-life of about 70 days in man, being decomposed through bacterial action to methane and mercury(0).

The environmental situation is complicated by the presence of species occurring naturally in aqueous and sedimentary conditions which are able to coordinate effectively with the organomercurials. For example, sulphur- or oxygen-containing ligands are known [14] to coordinate strongly with the CH_3Hg^+ species and thereby increase the solubility of these compounds in aqueous or organic systems. The known affinity of methylmercury compounds for sulphur-containing ligands has been used to ascribe [15,16] the attack of the organomercurials upon the cysteine residues of proteins, thereby causing failure in the sensory and motor functions of the central nervous system. It has also been suggested [9] that environmental pollution involving methylmercury toxins has been increased through the enhanced methylation of inorganic mercury compounds by coordination in natural waters containing sulphur.

Raman spectroscopic studies of CH_3HgONO_2 [17] and $ClCH_2HgONO_2$ [18] in aqueous solution have been used to determine the degree of dissociation of organomercury(II) nitrates to nitrate ions as a function of the species concentration. Formation constants for the methylmercury(II) cation coordinated with sulphate, sulphite, selenate and selenite ions in aqueous solution have also been obtained from ^1H NMR studies [19] and ^{199}Hg-proton coupling constants have been evaluated. In the present work, Raman spectroscopic studies of the methylmercury(II) species in solutions containing oxygen and sulphur donor ligands are described and, therefrom, a quantitative assessment of the presence of CH_3Hg^+ for oxygen- or sulphur-coordination is made.

2. Experimental

2.1. *Preparation of methylmercury(II) nitrate*

Methylmercury(II) chloride (BDH Chemicals Ltd.), 5.02 g, was shaken with an aqueous solution of silver nitrate, 3.40 g in 20 ml water, for 1 h in a stoppered flask. The silver chloride precipitate was filtered and the aqueous solution, which contained methylmercury(II) nitrate,

$$CH_3HgCl + AgNO_3 \rightarrow CH_3HgONO_2 + AgCl$$

was evaporated at room temperature under vacuum. The nitrate was recrystallized from water and dried under vacuum for 72 h; the yield of recrystallized CH_3HgONO_2 was 3.2 g, 57% of theoretical.

2.2. *Methylmercury(II) solutions*

Solutions of methylmercury(II) nitrate were made in dimethyl sulphide (1 *M*); dimethyl sulphoxide (0.5 *M*) and diethyl ether (0.5 *M*).

Anhydrous methylmercury(II) nitrate forms a 1:1 complex with dimethyl sulphide [14] and, although dimethyl sulphide itself is immiscible with water, the complex is soluble in water to form an approximately 1.3 *M* solution at 20 °C. 1.61 g of methylmercury(II) nitrate added to 0.45 ml of dimethyl sulphide and 4.55 ml of water produced a 1 *M* solution of the 1:1 complex. Progressive dilution of this solution produced 0.1 *M* and 0.01 *M* concentrations of the complex for spectroscopic study.

Solutions (0.5 *M*) of the complex in dimethyl sulphoxide and diethyl ether were prepared by the addition of 0.15 g of methylmercury(II) nitrate to 1 ml of the solvent.

2.3. *Raman spectra*

Raman spectra were excited by use of a Spectra-Physics Model 2020/5 argon ion laser operating at 488.0 nm with a nominal power of 1.0 W at this wavelength and recorded using a Spex Industries Model 1401 double monochromator with an EMI 9789 QA photomultiplier tube. The spectrometer scanning and data acquisition were controlled by use of a Nicolet 1180 computer and twin Diablo disk-drive system. The reciprocal linear dispersion of the spectrometer was 20.0 cm^{-1} mm^{-1} in the first order at 488.0 nm. The spectral slit width used in recording the spectra was 2 cm^{-1} and calibration was effected using the emission lines of a neon lamp. Vibrational wavenumbers were accurate to ± 1 cm^{-1}.

Sample temperatures could be maintained to better than ± 0.5 °C over the temperature range 0–30 °C with a Julabo F50HC circulatory system and a double-jacketed glass cell holder. The system has been described fully in an earlier paper [20].

To minimize errors arising from sample cell alignment for the samples under investigation, an internal standard, namely the ν(HgC) stretching fundamental band at about $\Delta\tilde{\nu} = 566$ cm^{-1}, was adopted. For each methylmercury solution, the Raman spectrum was recorded in the wavenumber region $\Delta\tilde{\nu} = 200$–650 cm^{-1} which encompassed the fundamental bands characteristic of ν(HgS), ν(HgO) and ν(HgC) stretching in the methylmercury species coordinated with sulphur- or oxygen-containing ligands.

Band areas were measured by use of the commercial CAP curve-resolution package on the Nicolet 1180 system and were accurate to $\pm 1\%$ for the stronger features and $\pm 5\%$ for the weakest bands.

3. Theory

Methylmercury(II) nitrate exists in organic solvents as the covalently bound species CH_3HgONO_2, which ionizes to the methylmercury(II) cation and nitrate ion:

$$CH_3HgONO_2 \rightleftharpoons CH_3Hg^+ + NO_3^-$$

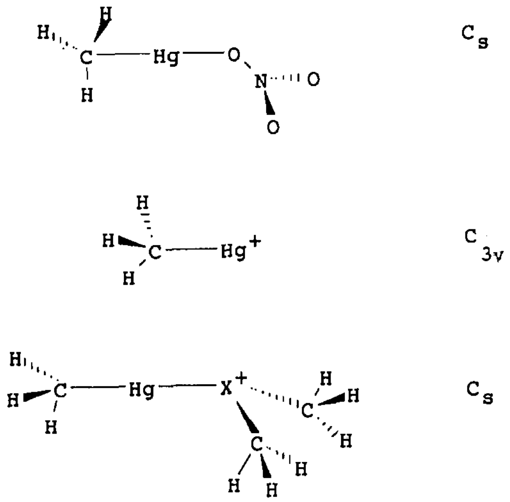

Fig. 1. Molecular structures of methylmercury(II) nitrate, the methylmercury(II) cation and the methylmercury(II) complex cation with coordinated $(CH_3)_2X$, where $X = O$, S.

In the presence of coordinating ligands such as $(CH_3)_2S$ and $(CH_3)_2O$ the CH_3Hg^+ ion forms the $(CH_3)_2XHgCH_3{}^+$ species, where X is O or S. The molecular symmetries of the CH_3HgONO_2, CH_3Hg^+ and $(CH_3)_2XHgCH_3{}^+$ [X = O, S] are described by the point groups C_s, C_{3v} and C_s, respectively (Fig. 1).

The simple CH_3Hg^+ cation belongs to the molecular point group C_{3v} for which

$$\Gamma_{\mathrm{vib}} = 3A_1 + 3E$$

and all vibrational modes are active in the Raman (3 polarized) and in the infrared spectrum. With a molecule containing oxygen or sulphur (donor atom X), the species CH_3HgX^+ now has

$$\Gamma_{\mathrm{vib}} = 4A_1 + 4E$$

for C_{3v} symmetry retention, i.e. with the assumption of linear CHgX bonding, and vibrational modes ν(HgX stretching) and δ(CHgX deformation) are obtained in addition to the six vibrational modes of the CH_3Hg^+ ion. For the oxygen and sulphur donor molecules considered here, namely $(CH_3)_2O$ and $(CH_3)_2S$, the symmetry point group of the $CH_3HgX(CH_3)_2{}^+$ species would be reduced to C_s, for which

$$\Gamma_{\mathrm{vib}} = 20A' + 16A''$$

However, a simplification of the molecular symmetry considerations is effected if we factor out the methyl group vibrations, and then we have

$$\Gamma_{\mathrm{vib}}^{\mathrm{CH_3}} = 14A' + 13A''$$

and $\Gamma_{\mathrm{vib}}^{\mathrm{skeletal}} = 6A' + 3A''$

With the assumption of freely rotating methyl groups, the skeletal structure of the $CH_3HgX(CH_3)_2{}^+$ ion consists of $CHgXC_2$, which has the molecular point group C_{2v} and then

$$\Gamma_{\mathrm{vib}}{}^{\mathrm{skeletal}} = 4A_1 + 2B_1 + 3B_2$$

Table 1

Vibrational wavenumbers and assignments for CH_3HgONO_2, aqueous solution

ν	Symmetry class	Wavenumber (cm^{-1})	Approximate description of vibrational mode
ν_1	A'	2944ms	CH_3 stretch
ν_2		2819w, bd	CH_3 stretch
ν_3		1422m, bd	CH_3 deformation
ν_4		1290m	NO_2 stretch
ν_5		1212s	CH_3 stretch
		1052vs	NO_3^- stretch
ν_6		1011w	NO stretch
ν_7		–	CH_3 rock
ν_8		760m	NO_2 deformation
		718mw	NO_3 deformation, NO_3^-
ν_9		–	NO_2 rock
ν_{10}		568vs	HgC stretch
ν_{11}		292m	HgO stretch
ν_{12}		170mw	HgON deformation
ν_{13}		–	CHgO deformation
ν_{14}	A''	3030vw	CH_3 stretch
ν_{15}		1505mw, bd	NO_2 stretch
ν_{16}		1422w	CH_3 deformation
ν_{17}	A''	–	CH_3 rock
ν_{18}		–	NO_2 rock
ν_{19}		–	NO_2 scissors deformation
ν_{20}		170mw	HgON deformation
ν_{21}		–	CHgO deformation
		464m, bd	$CH_3HgOH_2^+$, ν(Hg–O)

For both cases of C_s or C_{2v} molecular symmetry, nine skeletal vibrational modes would be active in the infrared and Raman, but with six and four bands polarized in the Raman spectrum for C_s and C_{2v} symmetry, respectively. Of the A_1 (C_{2v} symmetry) and A' (C_s symmetry) modes expected for the $CHgXC_2$ skeletal structure, the ν(Hg–C stretching), ν(Hg–X stretching), $\nu(XC_2$ symmetric stretching) and $\delta(XC_2$ deformation) are common to both point group vibrational analyses. In addition, for C_s symmetry the δ(CHgX deformation) and $\rho(XC_2$ rocking) are also of A' symmetry.

New skeletal features of A' or A_1 symmetry in the Raman spectrum of the $CH_3HgX(CH_3)_2^+$ species, in addition to those expected for the CH_3Hg^+ and $X(CH_3)_2$ moieties, are thus ν(HgX stretching), $\rho(XC_2$ rocking) and δ(CHgX deformation). In the quantitative spectroscopic assessment of the ligand coordination to the mercury atom, it is these vibrational modes which are considered; thereby, interference from vibrational features arising from uncoordinated CH_3Hg^+ or $X(CH_3)_2$ is minimized.

4. Results and discussion

The wavenumbers in the Raman spectrum of a 1 *M* aqueous solution of CH_3HgONO_2 are shown in Table 1. The presence of undissociated CH_3HgONO_2 as well as NO_3^- and $CH_3HgOH_2^+$ is clearly identified in Fig. 2; the assignments

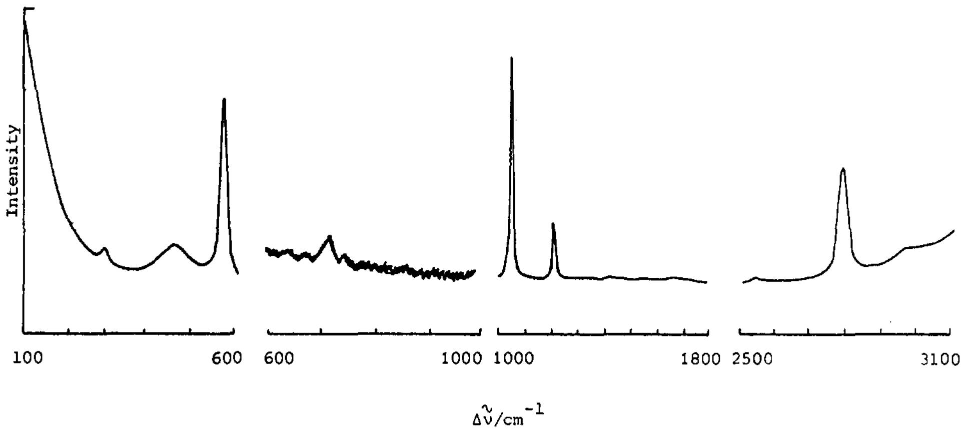

Fig. 2. The Raman spectrum, $\Delta\tilde{\nu} = 100\text{–}1800$ and 2500–3100 cm^{-1}, of a 1 *M* aqueous solution of CH_3HgONO_2.

in Table 1 are in essential agreement with those in the literature [14]. The important points to note for the present study are the ν(Hg–C) at 568 cm^{-1} for the CH_3HgONO_2 and $CH_3HgOH_2{}^+$ species [14] and the ν(Hg–O) of coordinated solvent in the $CH_3HgOH_2{}^+$ species at 464 cm^{-1}, which is considerably different from the similar mode in CH_3HgONO_2 at 292 cm^{-1}.

However, the Raman spectrum of methylmercury(II) nitrate in aqueous solution containing a 1:1 molar ratio of methylmercury(II) nitrate and dimethyl sulphide shows several differences which may be attributed to the coordination of $(CH_3)_2S$ to the mercury atom (Table 2). All of the nitrate is now confirmed to be ionic $NO_3{}^-$, with bands at 716, 1050 and 1384 cm^{-1}. The skeletal modes of the $CH_3HgS(CH_3)_2{}^+$ species are given in Table 2; a new polarized band at 302 cm^{-1} is assigned to ν(HgS) stretching of this complex and others at 180 and 130 cm^{-1} are assigned to the rocking modes of coordinated $(CH_3)_2S$. It should also be noted that the ν_1, ν_4 and ν_7 modes in Table 2 involve ν(CS) stretching and $\delta(CS_2)$ deformation modes which are shifted from their wavenumber positions in the free

Table 2

Vibrational wavenumbers and assignments for the skeletal modes of the $CH_3HgS(CH_3)_2{}^+$ species, C_s symmetry

Wavenumber (cm^{-1})		Symmetry class	Approximate description of vibrational mode	
680 (691) [a]	pol	A'	ν_1	CS symmetric stretch
546	pol		ν_1	Hg–C stretch
302	pol		ν_3	Hg–S stretch
291 (285) [a]	pol		ν_4	CS_2 deformation
180	pol		ν_5	CS_2 rock
–			ν_6	CHgS deformation
732 (742) [a]		A''	ν_7	CS asymmetric stretch
130			ν_8	CS_2 rock
–			ν_9	CS_2 torsion

[a] Corresponding wavenumbers of dimethyl sulphide [21] are indicated in parentheses.

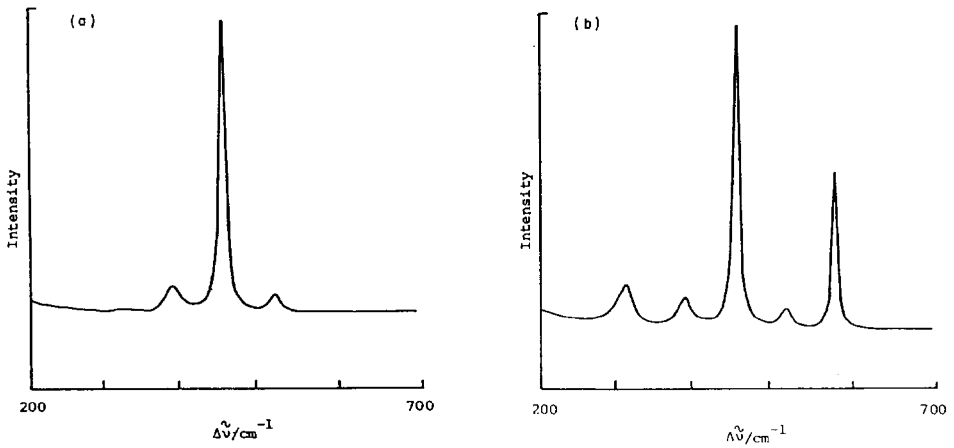

Fig. 3. The Raman spectra, $\Delta\tilde{\nu} = 200\text{–}700\ \text{cm}^{-1}$, of (a) diethyl ether, and (b) a 0.5 *M* solution of CH_3HgONO_2 in diethyl ether.

ligand. The ν_2 band in the complex, assigned to ν(Hg–C) stretching, occurs at 546 cm^{-1}, which is 22 cm^{-1} lower than its value in the aqueous cationic species $CH_3HgOH_2{}^+$. Of great significance here is the disappearance of the ν(Hg–O) band at 464 cm^{-1} in this aquo species. This means that $(CH_3)_2S$ competes so successfully with the oxygen donors H_2O and $NO_3{}^-$ in aqueous solution that it displaces them completely from coordination with CH_3Hg^+. There is no evidence for free dimethyl sulphide in this solution.

In the diethyl ether solution * of methylmercury(II) nitrate, the ν(HgC) is found at 562 cm^{-1} and the ν(HgO) of the ether-coordinated complex occurs at 308 cm^{-1} (Fig. 3).

In experiments designed to evaluate the competition between oxygen and sulphur donors for methylmercury(II) cations in solution, the 1 *M* aqueous solution containing 1 : 1 $CH_3Hg^+ : (CH_3)_2S$ was diluted 10 × and 100 × in water. The Raman spectra of dimethyl sulphide and of the complex in aqueous solution are shown in Fig. 4. There was no evidence for a ν(HgO) stretching band at 464 cm^{-1} indicative of mercury–oxygen coordination in the 0.1 *M* aqueous solution (Fig. 4c). However, in the 0.01 *M* aqueous solution, both the ν(HgS) and ν(HgO) bands at 303 and 464 cm^{-1} were visible (Fig. 4d), indicating that both mercury–oxygen and mercury–sulphur coordination were now present.

For the equilibrium between oxygen and sulphur donor species and methylmercury(II) cations in solution,

$$CH_3HgS(CH_3)_2{}^+ + OH_2 \rightleftharpoons (CH_3)_2S + CH_3HgOH_2{}^+$$

quantitative measurements of the Raman intensities of the ν(HgS) and ν(HgO) stretching bands will provide a measure of the relative ease of formation of the $CH_3HgS(CH_3)_2{}^+$ and $CH_3HgOH_2{}^+$ species.

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* In the present work, because of the different physical states of $(CH_3)_2O$ and $(CH_3)_2S$ at the temperature of our experiments — $(CH_3)_2O$ is a gas (b.p. −25 °C) and $(CH_3)_2S$ is a liquid (b.p. 38 °C) — $(C_2H_5)_2O$ (b.p. 35 °C) was used to demonstrate Hg–O coordination in solution.

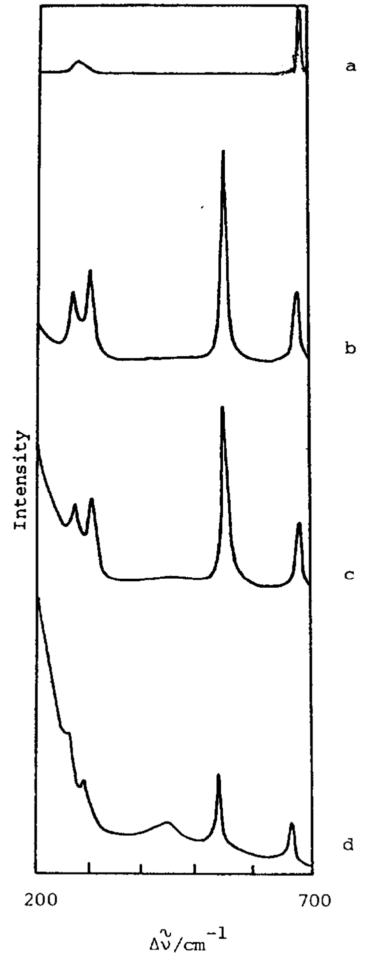

Fig. 4. The Raman spectra, $\Delta\tilde{\nu} = 200\text{–}700\ \mathrm{cm}^{-1}$, of (a) dimethyl sulphide, and of a 1 *M* 1 : 1 complex of dimethyl sulphide and methylmercury(II) nitrate in aqueous solution (b) 1 : 1 (c) 1 : 0 and (d) 1 : 100, complex : water.

The Raman band intensity is proportional to the concentration of scattering species [20] using an internal standard, which in this case is the ν(Hg–C) stretching band, to compensate for sample cell alignment and refractive index changes in the solution upon dilution. Hence,

$$I_x^{\mathrm{rel}} = J_x[x]$$

where I_x^{rel} is the measured relative band intensity of the ν(HgO), ν(HgS) and ν(HgC) standard bands for species x, namely $CH_3HgS(CH_3)_2^+$ and $CH_3HgOH_2^+$. Our calculations show that $J_S/J_O = 2.42$, which gives a measure of the relative scattering efficiencies J_S and J_O, respectively, of the $CH_3HgS(CH_3)_2^+$ and $CH_3HgOH_2^+$ species. This means that for equal molar concentrations of the sulphur- and oxygen-coordinated methylmercury(II) species in solution, the intensity of the ν(HgS) stretching band is 2.42 times that of the ν(HgO) stretching band.

In the 0.01 M aqueous solution of the 1:1 complex of dimethyl sulphide and methylmercury(II) cations, the actual relative intensity ratio of I_S^{rel} to I_O^{rel} is 1.50; this translates into a relative concentration of $[CH_3HgS(CH_3)_2{}^+]/[CH_3HgOH_2{}^+] = 0.60$ after application of the J_S/J_O factor calculated above. Thus, the equilibrium constant, K, for the displacement of dimethyl sulphide coordinated to methylmercury(II) cations by water may now be evaluated, since $K = \alpha^2 C/(1-\alpha)$ and $\alpha = 0.4$ for $C = 0.01$ mol dm^{-3}. A value of $K = 2.6 \times 10^{-3}$ mol dm^{-3} is calculated. Hence, it may be concluded that the coordination of methylmercury(II) to sulphur is about 2600 times more likely than its coordination to water for the $(CH_3)_2S$ and H_2O system. This result is of importance in studies of the environmental uptake of organomercurial compounds into biochemical cycles in the presence of sulphur-containing species. The increased toxicity of methylmercury(II) compounds in the presence of sulphur compounds has already been noted [15,16] in the literature. A decrease in the toxicity of organomercurials in the presence of selenium compounds has also been suggested [22–24] and it would be interesting to extend the present study to dimethyl selenide and methylmercury(II) nitrate in aqueous solution; on the basis of the present results it would be predicted that the ν(Hg–Se) stretching band intensity would diminish rapidly in the presence of excess H_2O for coordination.

The Raman spectrum of a 0.5 M solution of CH_3HgONO_2 in dimethyl sulphoxide requires further discussion since the expected coordination of sulphur to mercury does not occur *. The Raman spectrum (Fig. 5b) shows strong features assignable to ν(HgO) stretching and ν(HgC) stretching at 484 and 568 cm^{-1}, respectively, but there is no evidence for ν(HgS) stretching around 300 cm^{-1}. Also, unlike the dimethyl sulphide solution, the dimethyl sulphoxide complex of methylmercury(II) nitrate is unstable and the solution rapidly decomposes to give a black precipitate; this has been previously noted in the literature [14] and the precipitate is thought to be mercury(II) sulphide. We conclude therefore that the complex formed with methylmercury(II) nitrate in dimethyl sulphoxide is essentially different from that formed with dimethyl sulphide.

The value of the mercury–carbon stretching wavenumber, ν(Hg–C), has been proposed as a sensitive indicator of oxygen or sulphur bonding to mercury in methylmercury(II) complexes [19] and the value of 568 cm^{-1} found for the dimethyl sulphoxide solution found here is comparable with that found for the

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* Confirmation of Hg–O coordination of $MeHg^+$ to dimethyl sulphoxide might be provided by the examination of the ν(SO) stretching band wavenumbers of the free and coordinated ligands. However, the presence of the nitrate species in the DMSO solutions of CH_3HgONO_2 masks the ν(SO) stretching region in the Raman spectrum; the ν(SO) of the free ligand occurs at $\Delta\nu = 1042$ cm^{-1} in the Raman spectrum. A methyl rocking vibration also occurs at $\Delta\nu = 952$ cm^{-1}. A rather broad feature centred at 1045 cm^{-1} in DMSO solution of methylmercury(II) nitrate is difficult to interpret directly in terms of ligand ν(SO) shifts. Force-constant calculations (F.A. Cotton, W.D. Horrocks and R. Francis, *J. Phys. Chem.*, 64 (1960) 1534) show that the band assigned to ν(SO) stretching in DMSO contains only 46% SO stretching with substantial contributions from methyl deformation and rocking modes; this is supported by experimental observation of wavenumber shifts of up to 20 cm^{-1} for the ν(SO) band in metal complexes of DMSO and DMSO-d_6 (R.S. Drago and D. Meek, *J. Phys. Chem.*, 65 (1961) 1446). In contrast, the ν(CS) mode in DMSO is almost pure CS stretching. Evidence for mercury–oxygen coordination in a mercury(II) chloride complex with DMSO is provided by the infrared spectroscopic work of Selbin et al. (*J. Inorg. Nucl. Chem.*, 16 (1961) 219).

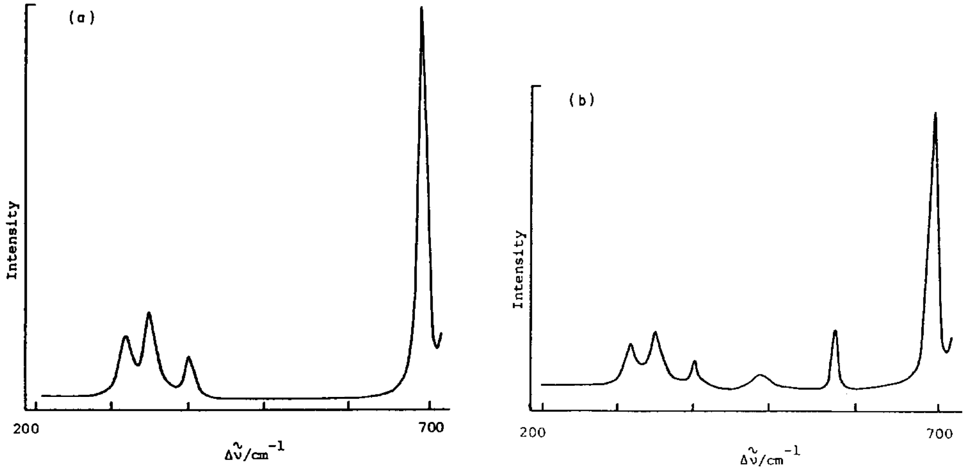

Fig. 5. The Raman spectra, $\Delta\tilde{\nu} = 200\text{–}700\ \mathrm{cm}^{-1}$ of (a) dimethyl sulphoxide and (b) a 0.5 *M* solution of methylmercury(II) nitrate in dimethyl sulphoxide.

coordination of selenite species to CH_3Hg^+, which has been studied by NMR and Raman spectroscopy [19], and which occurs with Hg–O ligand coordination. This provides further evidence for Hg–O coordination in the dimethyl sulphoxide complex of methylmercury(II) cations which we attribute to screening of the S^{VI} in the dimethyl sulphoxide.

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