

VIBRATIONAL SPECTRUM OF METHYLMERCURY(II) CYANIDE*

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INTRODUCTION

The stereochemistry of mercury(II) is proving of considerable interest as the number of structural determinations of its solid compounds increases¹. Of particular interest is the orientation of the two bonds in the two-covalent compounds. Diphenylmercury in the solid state is known² to have a linear C-Hg-C skeleton while dipole moment measurements³ on phenylmercury(II) cyanide in solution indicate that the skeleton is bent. The Raman spectrum of mercury(II) cyanide in methanol⁴ is interpreted on the linear skeleton model. The solid structure⁵, however, contains a CHgC angle of 171° due to Hg---N interaction between adjacent molecules.

Incomplete Raman spectra of methylmercury(II) halides have been reported by Fehér *et al.*⁶ and the results interpreted on the basis of an assumed linear C-Hg-X skeleton. A more recent study has been made by Goggin⁷. Microwave spectra⁸ of CH₃HgCl and CH₃HgBr and an X-ray structure analysis⁹ of CH₃HgCl show that the C-Hg-halogen skeleton is linear. Methylmercury(II) cyanide has been little investigated since its reported preparation¹⁰ and no structural studies have been published.

EXPERIMENTAL

CH₃HgI (prepared by sunlight irradiation of CH₃I and mercury¹¹) was shaken in methanol with freshly precipitated AgCN. The AgI was separated and the filtrate evaporated to dryness. The residue was dissolved in CHCl₃ and precipitated with n-hexane. Finally the solid was sublimed *in vacuo*. The white crystalline material (m.p. 93°, lit.¹⁰ 93°) was analysed. (Found: C, 10.0; H, 1.4; Hg, 82.5; N, 5.9. C₂H₃HgN calcd.: C, 9.95; H, 1.25; Hg, 83.0; N, 5.8 %.) Using the modified isothermal distillation method of Childs¹², the molecular weight of CH₃HgCN in 2 M acetone solution was found to be 264 (monomer weight is 241.5).

Raman spectra were photographed on Ilford Zenith plates with Hg 4358 Å using a Toronto arc source coupled to a Hilger E612 spectrograph and F/5.7 camera. Incident light was filtered through a saturated aqueous solution of NaNO₂. Plates were calibrated with the Fe arc spectrum and Raman shifts are considered accurate to ± 2 cm⁻¹ for sharp lines, and ± 5 cm⁻¹ for other features. Qualitative polarization

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information was obtained by the method of inserting cylinders of polaroid film between the source and sample tube.

Infrared spectra in the range 4000–300 cm^{-1} were recorded on a Perkin-Elmer Model 621 Spectrometer using mulls in Nujol and hexachlorobutadiene between KBr plates and polythene film.

RESULTS AND DISCUSSION

The Raman spectra of CH_3HgCN in the molten state (100°) and in representative solutions are listed in Table 1 together with the infrared spectrum of the solid. Solutions studied by the Raman effect and not included in Table 1 were methanol (4.7 M), acetonitrile (5.5 M) and tetrahydrofuran (6 M). In no case was a line attributable to CH_3HgCN -solvent interaction observed, nor could any broadening of solvent lines be detected. The frequency values altered on the average 10 cm^{-1} between the extremes, H_2O and $(\text{CH}_3)_2\text{S}$ as solvents. The order of change from higher to lower Raman shifts was $\text{H}_2\text{O} > \text{CH}_3\text{OH} \sim \text{C}_6\text{H}_6 \sim \text{CH}_3\text{CN} \sim \text{tetrahydrofuran} > (\text{CH}_3)_2\text{S} \sim \text{melt}$. The trend in $\Delta\bar{\nu}$ may reflect the change of concentration from lowest (H_2O) to highest $[(\text{CH}_3)_2\text{S}]$. No obvious correlation can be made with dielectric constants of the solvents. It follows from the relative constancy of values in Table 1 and the fact that stability constant measurements¹² indicate negligible ionic dissociation that an assignment may be made to vibrational modes of CH_3HgCN whose stereochemistry is apparently independent of the medium.

Assuming a linear C-Hg-C skeleton the molecular point group is C_{3v} . The vibrational modes are distributed between the symmetry species $5A_1 + 5E$, which are both infrared and Raman active. We observe in the Raman spectrum eleven lines of which six are polarized (Table 1). As will be discussed later, one of the polarized lines which is of very low intensity is difficult to account for, and without it, a complete and satisfactory assignment may be made. The assignment of frequencies (see Table 2)

TABLE 1
VIBRATIONAL SPECTRA OF CH_3HgCN

Raman ($\Delta\bar{\nu}$ cm^{-1})				Infrared (cm^{-1})		
H_2O (1.3 M)	C_6H_6 (2.4 M)	$(\text{CH}_3)_2\text{S}$ (9 M)	Melt	Description ^c	Solid (Mull)	Description ^c
^a	^a	^a	75	w, b, —	—	
306	303	304	303	s, dp	—	
386	383	379	377	s, p	374	vs
437	433	427	429	w, b, p	425	sd
565	563	558	561	vs, p	563	s, sh
800	^b	791	802	vw, b, dp	790	vs
1210	1205	1201	1202	s, p	1200	w, sh
1425	^b	^b	1419	w, dp	—	
2180	2174	2167	2168	s, p	—	
					2800	w
2929	2920	2915	2916	m, p	2920	s, sh
3007	^b	2991	3005	w, dp	2994	w

^a Masked by background. ^b Obscured by solvent lines. ^c w = weak, m = medium, s = strong, v = very, b = broad, sh = sharp, sd = shoulder, p = polarized, dp = depolarized.

TABLE 2

ASSIGNMENT OF FREQUENCIES OF CH_3HgCN TO C_{3v}

Sym. species	$\bar{\nu}$ (cm^{-1})	Approx. description of mode
A_1	2929	ν_1 C-H stretch
	2180	ν_2 C-N stretch
	1210	ν_3 CH_3 deformation
	565	ν_4 Hg- CH_3 stretch
	380	ν_5 Hg-CN stretch
E	3007	ν_6 C-H stretch
	1425	ν_7 CH_3 deformation
	800	ν_8 CH_3 rock
	306	ν_9 Hg-C-N bend
	75	ν_{10} C-Hg-C bend

is assisted by reference to the Raman spectra of $(\text{CH}_3)_2\text{Hg}^{14}$ and $\text{Hg}(\text{CN})_2^4$. The spectrum of the aqueous solution is treated.

Two C-H stretching frequencies are observed in the Raman spectrum at 2929 and 3007 cm^{-1} . The former must be assigned to ν_1 , since it is polarized, and 3007 cm^{-1} to ν_6 . The corresponding bands in the infrared occur at 2920 and 2994 cm^{-1} . The infrared band at 2800 cm^{-1} is attributed to the overtone of ν_7 which has gained intensity by Fermi resonance with ν_1 . The strong polarized line at 2180 cm^{-1} is assigned to the C-N stretching vibration. The value may be compared with 2189 cm^{-1} found for $\text{Hg}(\text{CN})_2$.

Degenerate methyl deformation frequencies for the methylmetal compounds generally fall in the range 1400-1450 cm^{-1} . Consequently, 1425 cm^{-1} is assigned to ν_7 . The corresponding vibration in $(\text{CH}_3)_2\text{Hg}$ occurs at 1443 cm^{-1} . The symmetrical methyl deformation (ν_3) of CH_3HgCN is represented by the strong, polarized line at 1210 cm^{-1} [cf. 1181 cm^{-1} in $(\text{CH}_3)_2\text{Hg}$] and by the band at 1200 cm^{-1} in the infrared [cf. 1205 cm^{-1} in $(\text{CH}_3)_2\text{Hg}$].

The weak broad line at 800 cm^{-1} lies in the region of methyl rocking frequencies when the methyl group is attached to a metal and it is assigned to ν_8 . The corresponding infrared band occurs at 790 cm^{-1} . The polarized Raman line at 565 cm^{-1} and the infrared band at 563 cm^{-1} must be assigned to the Hg- CH_3 stretching mode [cf. 515 cm^{-1} and 550 cm^{-1} for sym and asym $\nu(\text{Hg-C})$ in $(\text{CH}_3)_2\text{Hg}$].

Two polarized Raman lines remain to be assigned, 437 and 386 cm^{-1} , with only one totally symmetric mode to be accounted for, *viz.*, Hg-CN stretching. In $\text{Hg}(\text{CN})_2$ this mode is represented by a medium intensity line at 412 cm^{-1} . We select 386 cm^{-1} for ν_5 rather than the weak 437 cm^{-1} band because of its greater intensity. The assignment is supported by the occurrence in the infrared spectrum of an intense band at 374 cm^{-1} , while the counterpart of the Raman band at 437 cm^{-1} appears as a weak shoulder at 425 cm^{-1} .

The Raman bands at 306 and 75 cm^{-1} are assigned to ν_9 and ν_{10} respectively, by comparison with the Hg-C-N bending frequency in $\text{Hg}(\text{CN})_2$ (274 cm^{-1}) and C-Hg-C bending frequency in $(\text{CH}_3)_2\text{Hg}$ (160 cm^{-1}).

We have yet to account for the weak, polarized 437 cm^{-1} line. No suitable combination can be found for it, nor is it due to excitation by a Hg arc line other than

4358 Å. It may be disposed of by assigning it to ν_5 instead of 386 cm^{-1} and regarding the latter as the combination $\nu_9 + \nu_{10} = 381 (A_1 + A_2 + E)$. However, this explanation would make the combination band of much greater intensity than the fundamental. The relative intensities of 386 (strong) and 437 cm^{-1} (weak) rule out the possibility of Fermi resonance interaction of $\nu_9 + \nu_{10}$ with ν_5 .

Its constancy in all solutions and in the melt rules out solute-solvent interaction but not intermolecular interaction. The value 437 cm^{-1} lies in the range¹⁵ for $\nu(\text{Hg-N})$ so that it may be due to $\text{N} \rightarrow \text{Hg}$ interaction between adjacent molecules. The evidence does not support this possibility. Molecular weight determinations in acetone solution produced a value of 264 compared with the monomer weight of 241.5. $\text{Hg}(\text{CN})_2$ in the solid state is known⁵ to be polymeric with $\text{N} \cdots \text{Hg}$ bonds. However, no Raman line corresponding to 437 cm^{-1} was observed in aqueous and methanol solutions of $\text{Hg}(\text{CN})_2$ although the concentrations studied were significantly lower than those here. Because of the weakness of the line we were unable to obtain a definite result on measuring its relative intensity with change of concentration in a given solvent.

If $\text{Hg} \cdots \text{N}$ interaction were appreciable, one might expect two Raman lines in the C-N stretching region. When CH_3CN coordinates to metal halides $\nu(\text{C-N})$ in the infrared spectrum¹⁶ increases by 70–100 cm^{-1} . Raman spectra¹⁷ of solutions of ZnCl_2 and CH_3CN contain two C-N stretching frequencies at 2249 and 2312 cm^{-1} corresponding to free and complexed CH_3CN respectively.

So far we have not considered the possibility of the CH_3HgCN molecule having a non-linear C-Hg-C skeleton and C_s symmetry. In this case the degeneracy of the five E modes of the C_{3v} model is removed and ten polarized Raman lines are allowed. Clearly 437 cm^{-1} cannot be ascribed to a C-H stretching, CH_3 deformation or rocking mode. This leaves it to be assigned to the in-plane Hg-C-N bending vibration. C_s symmetry also requires that $\delta(\text{C-Hg-C})$ be polarized. The observed line at 75 cm^{-1} is of low intensity and lies so close to the exciting line that polarization measurements were not conclusive.

In view of the established linear configurations of C-Hg-N in the methylmercury(II) halides we favour the C_{3v} model for the cyanide. The following normal coordinate analysis was carried out on this basis.

TABLE 3

ASSUMED PARAMETERS OF CH_3HgCN

$r(\text{C-H})$	= 1.09 Å
$\angle \text{HCH}$	= $109^{\circ}28'$
$r(\text{Hg-CH}_3)$	= 2.05 Å
$r(\text{Hg-CN})$	= 1.99 Å
$r(\text{C-N})$	= 1.19 Å

TABLE 4

CALCULATED POTENTIAL CONSTANTS^a

1 sym C-H stretching	K_{11}^*	= 4.9
2 C-N stretching	K_{22}^*	= 17.5
3 sym CH_3 deforming	K_{33}^*	= 0.4
4 Hg- CH_3 stretching	K_{44}^*	= 2.8
5 Hg-CN stretching	K_{55}^*	= 2.1
6 asym C-H stretching	K_{66}^*	= 4.8
7 asym CH_3 deforming	K_{77}^*	= 0.5
8 CH_3 rocking	K_{88}^*	= 0.45
9 Hg-C-N bending	K_{99}^*	= 0.3
10 C-Hg-C bending	K_{1010}^*	= 0.15

^a Stretching constants in $\text{md}/\text{Å}$; bending constants in $\text{md}-\text{Å}$.

Normal coordinate calculation

The normal coordinate calculation was carried out by the Wilson FG-matrix method¹⁸ using a computer programme (FCLSQ; SD-9032 III) written by Schacht-schneider¹⁹. The molecular parameters listed in Table 3 were estimated from the known structures of CH_3HgCl , CH_3HgBr ⁸ and $\text{Hg}(\text{CN})_2$ ⁵. A linear C-Hg-C-N skeleton was assumed.

The principal moments [253.365 , 253.365 and 3.193×10^{-40} g-cm²] and the symmetrized G matrix were computed (SD-9064) from the assumed geometry and the following symmetry coordinates

$$\begin{array}{ll}
 S_1 = \Delta r_1 + \Delta r_2 + \Delta r_3 & S_9 = \Delta \alpha_2 + \Delta \alpha_3 - 2\Delta \alpha_1 \\
 S_2 = \Delta l_3 & S_{10} = \Delta \alpha_2 - \Delta \alpha_3 \\
 S_3 = \Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 - \Delta \alpha_1 - \Delta \alpha_2 - \Delta \alpha_3 & S_{11} = \Delta \beta_2 + \Delta \beta_3 - 2\Delta \beta_1 \\
 S_4 = \Delta l_1 & S_{12} = \Delta \beta_2 - \Delta \beta_3 \\
 S_5 = \Delta l_2 & S_{13} = \Delta \phi_1 \\
 S_6 = \Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 + \Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3 & S_{14} = \Delta \phi_2 \\
 S_7 = \Delta r_2 + \Delta r_3 - 2\Delta r_1 & S_{15} = \Delta \theta_1 \\
 S_8 = \Delta r_2 - \Delta r_3 & S_{16} = \Delta \theta_2
 \end{array}$$

where r_1 is the length of the C-H₁ bond; $r_2 = \text{C-H}_2$; $r_3 = \text{C-H}_3$; α_1 is the angle H₂-C-H₃ etc.; β_1 is the angle H₁-C-Hg etc.; $l_1 = \text{Hg-CH}_3$; $l_2 = \text{Hg-CN}$; $l_3 = \text{C-N}$; θ is the angle C-Hg-C; ϕ is the angle Hg-C-N.

The calculation using a simple valence force field gave exact agreement between the calculated and observed frequencies. The resulting force constants are listed in Table 4. The values do not differ significantly from those obtained for $\text{Hg}(\text{CN})_2$ ^{4,20} and $\text{Hg}(\text{CH}_3)_2$ ²¹. The potential energy distribution is shown in Table 5.

TABLE 5
POTENTIAL ENERGY DISTRIBUTION

Mode	K_{11}	K_{22}	K_{33}	K_{44}	K_{55}	K_{66}	K_{77}	K_{88}	K_{99}	K_{1010}
r_1	0.997		0.001	0.001						
r_2		0.964			0.036					
r_3			0.922	0.076						
r_4			0.076	0.910	0.013					
r_5		0.036		0.012	0.951					
r_6						0.996	0.003			
r_7							0.963	0.034		
r_8							0.034	0.964		
r_9									0.947	0.053
r_{10}									0.053	0.946

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SUMMARY

Raman spectra of CH_3HgCN in the melt and in solutions of a range of solvents including H_2O , $(\text{CH}_3)_2\text{S}$ and C_6H_6 have been obtained. Minor changes in the frequencies with medium were observed. The infrared spectrum of the solid has been recorded between 4000 and 300 cm^{-1} . A complete assignment to vibrational modes corresponding to C_{3v} and a normal coordinate analysis based on a simple valence force field have been made.

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