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# Vibrational Spectra and Normal Coordinate Analysis of Bis(methylthio)mercury

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The IR and Raman spectra of bis(methylthio)mercury and methyl(methylthio)mercury were studied. Fundamental vibrations were assigned as follows: frequencies 698, 330, 530 and 174 cm$^{-1}$ to C–S stretching, S–Hg stretching, C–Hg stretching and C–S–Hg bending vibrations, respectively. The fundamental vibrations were confirmed by normal coordinate analysis. The force constants of S–C and S–Hg stretching vibrations were estimated to be 2.16 and 1.5 md/Å, respectively.

Irukayama *et al.*[1] reported on the IR spectra of ethyl(methyl)mercury, bis(ethylmercury)sulfide, and bis(ethylthio)mercury in NaCl region. Since sulfur atoms greatly contribute to formation of complexes between mercury and proteins such as cystine in a living body, it seems important to find also in the biochemical field vibrational bands characteristic of S–Hg and C–Hg linkages. We have carried out spectroscopic studies on a series of alkylmercury compounds containing sulfur.

Assignment of the IR and Raman spectra of bis(methylthio)mercury $(MeS)_2Hg$ and methyl(methylthio)mercury MeHgSMe was made in order to get information on S–Hg and C–Hg bond vibrations. Molecular structure was discussed. Bradley and Kuncher[2] determined the geometry of $(MeS)_2Hg$ by X-ray diffraction. They concluded that a skeletal S–Hg–S bond was linear in form and methyl groups at both ends were oriented in *trans* around S–Hg–S bond, but the conformations of hydrogens could not be determined. We have confirmed the assignment by normal coordinate analysis.

## Experiment

$(MeS)_2Hg$ and MeHgSMe were prepared by the methods of Wertheim[3] and Kondo,[4] respectively. The mp and IR spectra were in good agreement with those given by them.

Instruments used for IR measurements were a JASCO-DS 403G grating infrared spectrophotometer from 4000 to 250 cm$^{-1}$ and a FIS-3 Hitachi far infrared spectrophotometer from 400 to 30 cm$^{-1}$. IR spectra of $(MeS)_2Hg$ were measured by the KBr disk method in the region 4000—400 cm$^{-1}$ and Nujol method in the far IR region. Raman spectrum was measured in powder state. Measurements of IR and Raman spectra of MeHgSMe were carried out in liquid state(mp 25 °C).

## Assignment

Band assignments were made by comparing the spectra of $(MeS)_2Hg$ with those of MeHgSMe and $Me_2Hg$. It was assumed that the structure of MeHgSMe belongs to the $C_s$ point group. Assignment of $Me_2Hg$ was made in reference to Gutowsky's investigation.[7] The vibrational modes of Me group and the remaining skeleton were discussed. Observed vibrational spectra are shown in Figs. 1—5.

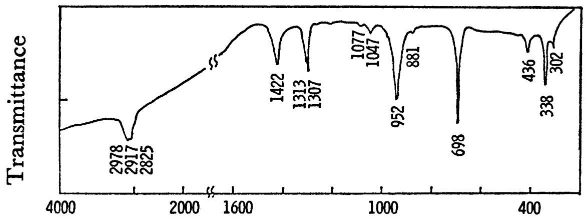

Fig. 1. Observed infrared spectrum in the 4000—300 cm$^{-1}$ region for $(MeS)_2Hg$.

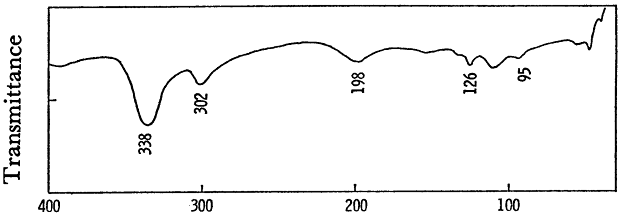

Fig. 2. Observed far-infrared spectrum for $(MeS)_2Hg$.

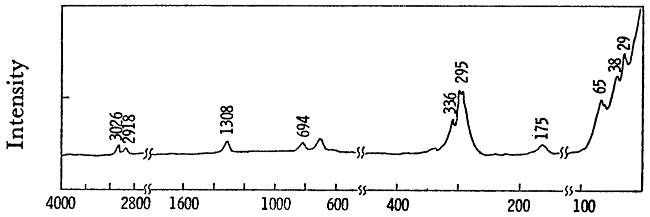

Fig. 3. Observed Raman spectrum of $(MeS)_2Hg$.

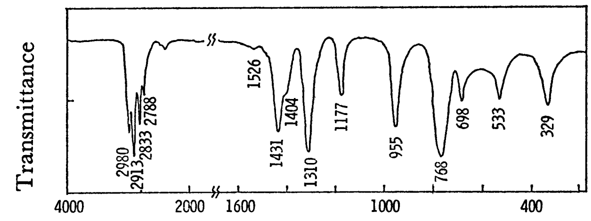

Fig. 4 Observed infrared spectrum for MeHgSMe.

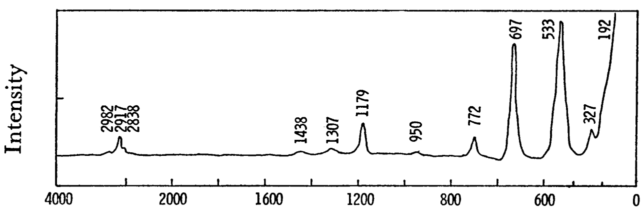

Fig. 5. Observed Raman spectrum of MeHgSMe.

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*Methyl Group Fundamental Frequencies.* Assignment of degenerate and symmetric stretching frequencies of Me group is straightforward. It is well-known that the bands of Me group deformation vibrations occur near 1400, 1300 and 1000 cm$^{-1}$. It can be predicted that the bands observed for both $(MeS)_2Hg$ and MeHgSMe are due to the Me group attached to sulfur atom (Me–S) and those for both MeHgSMe and $Me_2Hg$ are due to the Me group attached to mercury atom (Me–Hg).

The frequencies of 1422, 1313 and 952 cm$^{-1}$ in $(MeS)_2Hg$ were thus assigned to degenerate deformation, symmetric deformation and rocking vibrations of the former, respectively. The frequencies are in good correspondence with the frequencies 1432, 1307 and 950 cm$^{-1}$ in dimethyldisulfide[5] and 1432, 1322 and 964 cm$^{-1}$ in methylmercaptane.[6] Similarly, IR bands at 1404, 1177 and 768 cm$^{-1}$ in MeHgSMe were assigned to the deformation vibrations of the latter. The splitting was observed at the symmetric deformation band of Me–S in $(MeS)_2Hg$ as in $Me_2GeO$, the reason not being known.

*Skeletal Fundamental Frequencies.* The band at 698 cm$^{-1}$ in $(MeS)_2Hg$ and MeHgSMe can be assigned to C–S stretching vibration.

Gutowsky[7] suggested that C–Hg stretching frequency was 550 cm$^{-1}$ in IR and 515 cm$^{-1}$ in Raman spectra of $Me_2Hg$. Goggin and Woodward[8] also observed C–Hg stretching bands at 538—546 cm$^{-1}$ and Cl–Hg stretching band at 313 cm$^{-1}$ in IR spectra of MeHgX (X=Cl, Br and I). The results indicate that S–Hg stretching bands might appear in the range 500—200 cm$^{-1}$. Strong bands are observed near 330 cm$^{-1}$ for $(MeS)_2Hg$ and MeHgSMe but not $Me_2Hg$. $(MeS)_2Hg$ exhibits anti-symmetric($B_u$) and symmetric($A_g$) stretching vibrations of S–Hg–S bond at 338 cm$^{-1}$ in IR and 295 cm$^{-1}$ in Raman spectra. The weak bands at 336 cm$^{-1}$ in Raman and 302 cm$^{-1}$ in IR seem to be essentially forbidden, since their frequencies are very close to the allowed ones.

Similarly the IR absorption band at 198 cm$^{-1}$ and Raman shift of 175 cm$^{-1}$ in $(MeS)_2Hg$ are assigned to anti-symmetric($B_u$) and symmetric($A_g$) C–S–Hg bending vibrations, respectively. In the region below 150 cm$^{-1}$, frequencies 126 and 95 cm$^{-1}$ (Fig. 2) are regarded to be the fundamental bands of S–Hg–S bending vibrations($A_u$ and $B_u$), since their combinations are most consistent with the observed values 1077 and 1047 cm$^{-1}$. It is assumed that the Raman shifts of 65, 38 and 29 cm$^{-1}$ (Fig. 3) are assigned to the torsional vibration of methyl group around S–Hg–S axis or lattice vibrations.

## Results and Discussion

Normal coordinate treatment for $(MeS)_2Hg$ was performed using the molecular geometry shown in Fig. 6 ($C_{2h}$). Normal vibrations of species constitute $8A_g+6A_u+4B_g+9B_u$. Molecular parameters of skeleton were taken from results of X-ray diffraction.[2] The methyl group was regarded to be tetrahedral.[10] Thus, bond distances(Å): Hg–S, 2.36; S–C 1.70; C–H 1.09, bond angles(degree): S–Hg–S 180; Hg–S–C 111; S–C–H 109.5; H–C–H 109.5.

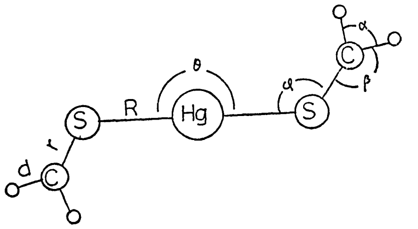

Fig. 6. Molecular geometry of $(CH_3S)_2Hg$ ($C_{2h}$).

The internal rotations of Me groups and the torsional vibrations about S–Hg–S axis were neglected since they possessed frequencies low enough to be separated. A computer program by Shimanouchi[11] and modified for this work was used for carrying out the numerical calculations with the GF matrix method. The potential function employed was based on a modified Urey-Bradley force field. It was necessary to introduce an intramolecular tension term[12] to bring the calculated frequencies close to the observed ones. Repulsive force between non-bonded S and S atoms was ignored.

TABLE 1. MODIFIED UREY-BRADLEY FORCE CONSTANTS FOR BIS(METHYLTHIO)MERCURY (md/Å)

| | I | II | | III | | IV | | V | |
|---|---|---|---|---|---|---|---|---|---|
| | | FC | $\phi$ | FC | $\phi$ | FC | $\phi$ | FC | $\phi$ |
| K(CH) | 4.56 | 4.566 | 0.003 | * | | 4.566 | 0.004 | * | |
| K(SC) | 2.17 | 2.159 | 0.016 | * | | 2.170 | 0.017 | * | |
| K(SHg) | 1.50 | 1.492 | 0.030 | * | | 1.587 | 0.022 | * | |
| H(HCH) | 0.389 | 0.389 | 0.001 | * | | 0.390 | 0.001 | * | |
| H(HCS) | 0.246 | 0.247 | 0.001 | * | | 0.248 | 0.001 | * | |
| H(CSHg) | 0.140 | 0.127 | 0.005 | * | | 0.109 | 0.005 | * | |
| H(SHgS) | 0.122 | | | | | 0.122 | 0.005 | * | |
| F(H:H) | 0.085 | * | | 0.086 | 0.002 | * | | 0.087 | 0.002 |
| F(H:S) | 0.298 | * | | 0.304 | 0.004 | * | | 0.304 | 0.006 |
| F(C:Hg) | 0.130 | * | | 0.104 | 0.010 | * | | 0.071 | 0.012 |
| Kappa** | −0.057 | * | | −0.058 | 0.002 | * | | −0.058 | 0.003 |

$\phi$) dispersion. I) starting values; II), III) refined for $A_g$ and $B_g$ species; IV), V) refined for $A_u$ and $B_u$ species. * As in column I. ** md·Å.

At first contributions of the force constants concerned with mercury atom to the calculated frequencies were estimated. Final adjustments of all the force constants were accomplished by the Jacobian matrix.[11]

The MUBF constants given in Table 1 fall in a reasonable range, *e.g.*, for alkyl sulfide[13] $K$(C–S)=1.75, $H$(HCS)=0.17, $K$(C–H)=4.250, and $H$(HCH)=0.37 md/A.

$K$(Hg–S) in question is evaluated to be 1.5 md/Å. Cooney and Hall[14] measured the Raman spectra of sodium sulfide mercury $Na_2HgS_2$, in which only a single line was observed at 352 cm$^{-1}$. The data and the result of X-ray investigation suggest that the ion $HgS_2^{2-}$ is linear in form. For a linear XYX-type molecule, the symmetric stretching frequency is approximately given by

$$\nu = 1303.16[(K+2F)/\mu N]^{1/2}$$

where $K$ and $F$ are stretching and repulsive force constants, respectively. Substituting 352 cm$^{-1}$ into $\nu$, we obtain 2.02 md/Å for the value of $K+2F$, which is slightly greater than 1.5 md/Å in Table 1.

In the Gordy rule,[15] which is simple and applicable to various molecules,

$$K_G = 1.67N(x_A x_B/d^2)^{3/4} + 0.30$$

where $N$ is the bond order, $x_A$ and $x_B$ are the electronegativities of bonded atoms A and B, respectively, $d$ is bond distance at equilibrium and $K_G$ is the stretching force constant. Since potential energy distribution(PED) for Hg-S and S-C stretching coordinates are nearly 100% (Table 2), the evaluation of $K_G$(Hg–S) and $K_G$(S–C) was attempted, the results being 1.22 and 3.35 md/Å, respectively, for the values 1.5 and 2.17 md/Å in Table 2.

TABLE 2. CALCULATED AND OBSERVED VIBRATIONAL FREQUENCIES (cm$^{-1}$)

| Calcd | Obsd | Assignment |
|---|---|---|
| $A_g$ species | | |
| 2978 | 2978 | C-H asym str |
| 2917 | 2917 | C-H sym str |
| 1422 | 1422 | Me deg deform |
| 1310 | 1308 | Me sym deform |
| 954 | 952 | Me rock |
| 694 | 694 | S-C str |
| 295 | 295 | Hg-S str |
| 175 | 175 | C-S-Hg bend |
| $A_u$ species | | |
| 2978 | 2978 | C-H asym str |
| 1422 | 1422 | Me deg deform |
| 949 | 952 | Me rock |
| 130 | 126 | S-Hg-S out-of-plane bend |
| $B_g$ spcies | | |
| 2978 | 2978 | C-H asym str |
| 1421 | 1422 | S-C str |
| 948 | 952 | Me rock |
| $B_u$ species | | |
| 2977 | 2978 | C-H asym str |
| 2917 | 2917 | C-H sym str |
| 1422 | 1422 | Me deg deform |
| 1311 | 1310 | Me sym deform |
| 954 | 952 | Me rock |
| 698 | 698 | S-C str |
| 338 | 338 | Hg-str |
| 198 | 198 | C-S-Hg bend |
| 88 | 95 | S-Hg-S in-plane bend |

The calculated frequencies are in good agreement with those observed within experimental error (Table 2). Repeated calculations showed a reproducible tendency for $A_g$ frequency to be lower than $B_u$ for Hg-S stretching vibrations and $A_u$ frequency higher than $B_u$ for S-Hg-S bending vibrations. The frequency 126 cm$^{-1}$ was thus assigned to $A_u$ rather $B_u$. Ambiguity in assignment near 100 cm$^{-1}$ region did not affect the resulting values of force constants so much.

Each PED located to one symmetry coordinate is given in Table 2. It is also possible to employ a local symmetry force field instead of MUBFF. Some normal coordinates which mix two kinds of symmetry coordinate indicate total PED exceeding 100%. This is due to negligence of the negative PED contributions or cross terms.

The selection rules indicate that methyl groups at both ends have *trans* conformation with respect to the S–Hg–S bond. Normal coordinate analysis of $(MeS)_2Hg$ was made on the basis of $C_{2h}'$ point group. Using MUBFF, K(S–Hg), H(CSHg) and H(SHgS) were evaluated to be 1.5, 0.11 and 0.122 md/Å, respectively. Separation into group vibrations was satisfactory.

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