

ing motion. We interpret the 408-cm<sup>-1</sup> band as the expected A<sub>1</sub> mode in both HMn(CO)<sub>5</sub> and DMn(CO)<sub>5</sub>. The assignments of the middle-frequency bands are given in Table I.

In making the assignments of several combination bands in the high-frequency region, it was recognized that there are three strong fundamentals expected in the low-frequency region. Since three of these combination bands are difference bands, we found that the low-frequency bands are at 120, 106, and 77 cm<sup>-1</sup>. The analogous bands in Mn(CO)<sub>5</sub>X (X = Cl, Br, I) occur as follows: E (120–126 cm<sup>-1</sup>), E (100–106 cm<sup>-1</sup>), and A<sub>1</sub> (58–63 cm<sup>-1</sup>).

### Discussion

In order to test the present assignment, the Teller-Redlich isotope products can be compared with the theoretical requirements. These requirements are found by taking into account not only the changes in vibrational reduced masses which occur upon substitution of D for H but also the concomitant changes in total mass and moments of inertia. Assuming that the geometry of the Mn(CO)<sub>5</sub> moiety is the same in the vapor as in the solid and taking the Mn-H distance as 1.3 Å (a number in some dispute but to which only *I<sub>x</sub>* and *I<sub>y</sub>* are only very slightly sensitive), one finds the re-

quired products, including the relevant translations and rotations, to be

$$(A_1) \prod_{i=1}^7 \frac{\nu_i^H}{\nu_i^D} = 1.411; (E) \prod_{i=1}^8 \frac{\nu_i^H}{\nu_i^D} = 1.402$$

The products calculated from the present assignments are

$$(A_1) \quad \Pi = 1.403 \qquad (E) \quad \Pi = 1.418$$

While the value for the A<sub>1</sub> modes fulfills the requirement well, the value for the E modes is slightly above expectation. It is quite likely that the explanation of this variation involves a Fermi resonance effect to be expected on the basis of the rather great vibrational anharmonicities of motions involving H and D and the presence in the middle-frequency region of the combination band of E symmetry species.

We conclude that the spectrum of HMn(CO)<sub>5</sub> is understandable on the basis of C<sub>4v</sub> symmetry, which the molecule is known to have in the solid state, and that it is not necessary to assume lower symmetry, such as C<sub>s</sub> or C<sub>2v</sub>, to explain the entire spectrum.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
ILLINOIS INSTITUTE OF TECHNOLOGY, TECHNOLOGY CENTER, CHICAGO, ILLINOIS 60616

## Infrared, Raman, and Proton Magnetic Resonance Spectra of Dicyclopentadienylmercury and Related Compounds<sup>1,2</sup>

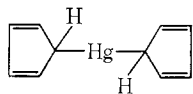
BY E. MASLOWSKY, JR.,<sup>3a</sup> AND KAZUO NAKAMOTO

Received October 31, 1968<sup>3b</sup>

The infrared and Raman spectra of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Hg and (C<sub>5</sub>H<sub>5</sub>)HgX types of compounds (X = halogen) have been compared with those of C<sub>5</sub>H<sub>6</sub>. It has been concluded that the Hg atoms of these compounds are σ bonded to the C<sub>5</sub>H<sub>5</sub> rings. In (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Hg, the C-Hg-C bond is linear and the antisymmetric and symmetric Hg-C stretching vibrations are assigned at 348 and 321 cm<sup>-1</sup>, respectively. However, the relative orientation of the C<sub>5</sub>H<sub>5</sub> rings could not be determined, since there was no appreciable vibrational coupling between the vibrations of the two C<sub>5</sub>H<sub>5</sub> rings.

### Introduction

Originally, dicyclopentadienylmercury was formulated as containing the mercury atom bonded to the carbon atoms of the cyclopentadienyl rings by means of σ bonds.<sup>4</sup> The π-bonded structure such as that found



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(2) To be submitted by E. M. to the faculty of Illinois Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) (a) Supported by an NDEA fellowship during this investigation. (b) Revised March 25, 1969.

(4) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956).

in ferrocene was rejected since the infrared spectrum of this compound is much more complex than that of ferrocene. However, its pmr spectrum at room temperature consists of a single sharp peak ( $\tau$  4.2), which is indicative of the π-bonded structure. To reconcile these conflicting results, Piper and Wilkinson<sup>5</sup> proposed that, while the mercury atom is indeed σ bonded to the ring, the point of attachment changes at such a rate that the protons on the ring appear equivalent in the pmr spectrum (valence tautomerism). Recently, Nesmeyanov, *et al.*,<sup>6</sup> questioned the σ-bonded structure; in addition to the pmr evidence mentioned above, they

(5) T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

(6) A. N. Nesmeyanov, G. G. Dvoryantseva, N. S. Kochetkova, R. B. Materikova, and Y. N. Sheinker, *Dokl. Akad. Nauk SSSR*, **169**, 847 (1964)

claimed that the infrared spectrum is too complex even for the  $\sigma$ -bonded structure and that the uv spectrum cannot be accounted for on the basis of the  $\sigma$ -bonded structure. They vaguely proposed a structure which involves both  $\sigma$  and  $\pi$  bonding or bonding intermediate between them. Also, Cotton<sup>7</sup> has recently suggested that a structure involving allylic bonding of the mercury atom to the cyclopentadienyl rings seems attractive.

X-Ray diffraction would be the logical tool for determining the structure of dicyclopentadienylmercury. It is extremely difficult, however, to grow single crystals of this compound. In addition, the compound decomposes quite readily on exposure to light. It was therefore decided to study this compound further using infrared, Raman, and pmr spectroscopy as the main tools, in the hope of proposing a structure which is consistent with the experimental data.

### Experimental Section

Dicyclopentadienylmercury,  $(C_5H_5)_2Hg$ , was prepared using the method of Wilkinson and Piper.<sup>4</sup>  $(C_5H_5)HgCl$  was prepared according to the method of Nesmeyanov, *et al.*<sup>6</sup> To 0.831 g of dicyclopentadienylmercury (2.51 mmol) in 10 ml of THF was added 0.683 g of  $HgCl_2$  (2.51 mmol) in 15 ml of THF. The mixture was kept in a stoppered flask for 0.5 hr. The solvent was then removed using a rotary evaporator. To the residue was added 20 ml of absolute ethanol. This solution was heated on a water bath, then filtered, and cooled in a Dry Ice-acetone bath. A light yellow solid was collected. The compound is quite stable, when contrasted with dicyclopentadienylmercury, which begins to decompose after several hours when left in the presence of air and light. The compounds  $(C_5H_5)HgBr$  and  $(C_5H_5)HgI$  were prepared in an analogous manner, using  $HgBr_2$  and  $HgI_2$ .

Cyclopentadiene,  $C_5H_6$ , was prepared by pyrolysis of dicyclopentadiene (purchased from Eastman Organic Chemicals), using a 250-ml flask fitted with a fractionating column, 25 cm long and 1 cm in diameter, packed with glass rings, 0.5 cm in diameter. The column was connected to a vertical condenser. The monomer was condensed at about 41° and was collected in a receiver cooled in a Dry Ice-acetone bath, where it was stored until needed.

The infrared spectra were measured by using a Beckman IR-12 (4000–200  $cm^{-1}$ ) and a Beckman IR-11 (400–33  $cm^{-1}$ ) spectrophotometer. The frequencies were calibrated using polystyrene and water vapor. The spectral resolution was approximately 2  $cm^{-1}$  with an accuracy of  $\pm 1$   $cm^{-1}$ . The solution spectra were run using CsBr and polyethylene cells, with cyclohexane, carbon disulfide, and chloroform as solvents. The solid-state spectra were obtained in Nujol and perfluorocarbon mulls and KBr pellets. The Raman spectra were measured using a Cary Model 81 spectrophotometer with an He-Ne gas laser attachment and calibrated using the helium and argon discharge lines. The solid samples were investigated by collecting the light scattered at 180° from the sample, which was held in a sealed soft-glass ampoule containing a nitrogen atmosphere. The solution spectra were run in a capillary tube, using carbon tetrachloride, chloroform, and carbon disulfide as solvents. Since  $(C_5H_5)_2Hg$  is light sensitive, some difficulty was encountered in measuring the infrared and Raman spectra. The rate of decomposition depended on how soon the spectra were obtained after preparing a sample of the compound. If the spectrum was taken immediately after preparation, the decomposition was much less than if the sample had been stored for 1 day at Dry Ice temperature and in an inert atmosphere, in which case decomposition would begin

immediately on exposure to the atmosphere. To ensure that any peaks observed were not due to decomposition products, the samples were run at different time intervals after preparation and therefore in different states of decomposition, to observe any changes in the relative intensity of the peaks in the spectrum. The pmr spectra were measured using a Varian A-60 spectrophotometer with a variable-temperature attachment. Sulfur dioxide, diethyl ether, tetrahydrofuran, and carbon disulfide were used as solvents. The temperature was calibrated by measuring the separation in the methanol peaks.

### Results and Discussion

Consider first the manner of attachment of the mercury atom to the cyclopentadienyl rings. As is shown in Figure 1, at least three types of bonding schemes can be proposed. The first is that found in ferrocene where the metal atom is  $\pi$  bonded to the center of the cyclopentadienyl rings (A). Another is of a  $\pi$ -allylic type (B) as was recently proposed for  $(C_5H_5)_2Mo(NO)I$  and  $(C_5H_5)_2Mo(NO)CH_3$ .<sup>8</sup> The last is of the  $\sigma$ -bonded type (C) found in such compounds as  $(C_5H_5)_3Al$  and  $(C_5H_5)_3Si(CH_3)_3$ .<sup>9</sup>

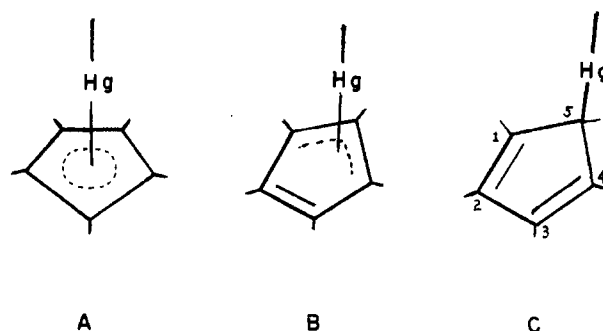


Figure 1.—Three possible types of bonding schemes involving the mercury atom and the  $C_5H_5$  rings:  $\pi$ -type structure (A),  $\pi$ -allylic structure (B), and  $\sigma$ -type structure (C).

The infrared spectrum of  $(C_5H_5)_2Hg$  is much too complicated to be explained in terms of a sandwich-type structure.<sup>10</sup> The  $\pi$ -allylic structure seems very unlikely. At present it has only been proposed for the two molybdenum compounds mentioned earlier. The basis for proposing this as a possible structure was the number of electrons needed in order for the molybdenum atom to attain an inert gas electronic structure. On comparing the infrared spectrum of  $(C_5H_5)_2Mo(NO)I$  with that of  $(C_5H_5)_2Hg$ , it is seen that they are essentially different. A portion of these spectra together with a portion of the spectra of  $C_5H_6$  are shown in Figure 2. On the basis of the infrared spectra, the  $\pi$ -allylic structure is ruled out for  $(C_5H_5)_2Hg$ .

The  $\sigma$ -bonded structure is chosen mainly on the basis of a comparison of the infrared spectrum of  $(C_5H_5)_2Hg$  with that of  $C_5H_6$ . The structure of the cyclopentadienyl rings of the mercury compound differs from that of cyclopentadiene only in that a hydrogen atom on the C(5) carbon of the cyclopentadienyl ring has been replaced by a mercury atom. The spectra of these two compounds should be very similar. Special attention

(8) R. B. King, *Inorg. Chem.*, **7**, 90 (1968).

(9) K. C. Frisch, *J. Am. Chem. Soc.*, **75**, 6050 (1953).

(10) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

(7) F. A. Cotton, "Proceedings of the Robert A. Welch Foundation. IX. Organometallic Compounds," W. O. Mulligan, Ed., 1966, p 213.

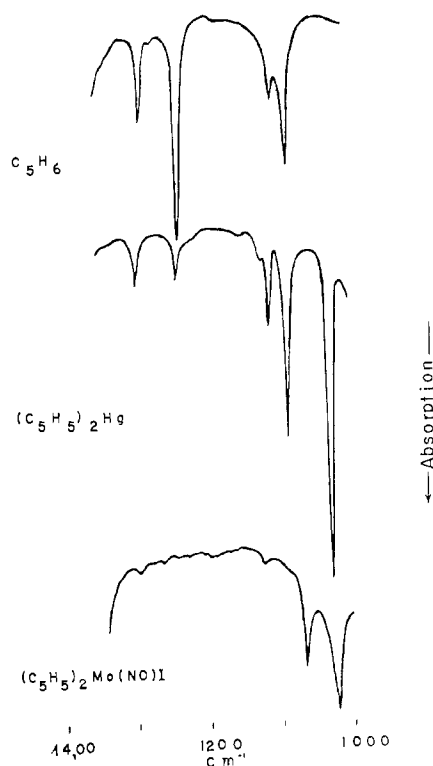


Figure 2.—The infrared spectra of  $C_5H_6$ ,  $(C_5H_5)_2Hg$ , and  $(C_5H_5)_2Mo(NO)I$  in a carbon disulfide solution between 1000 and 1350  $cm^{-1}$ .

should be paid to the region where  $C=C$  stretching vibrations appear. This has been assigned to a peak at 1500  $cm^{-1}$  in cyclopentadiene.<sup>11</sup> A band at 1530  $cm^{-1}$  is assigned to the  $C=C$  stretching vibration in  $(C_5H_5)_2Hg$ . As can be seen in Figure 3, the spectra of these two compounds are essentially identical in this region.

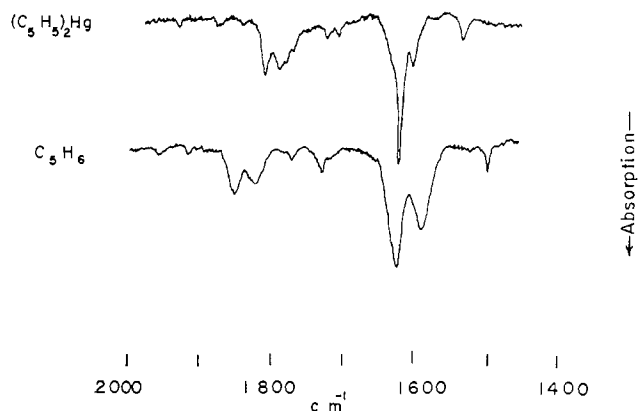


Figure 3.—The infrared spectra of  $(C_5H_5)_2Hg$  and  $C_5H_6$  in a hexane solution between 1450 and 2000  $cm^{-1}$ .

It has been argued that the infrared spectrum of  $(C_5H_5)_2Hg$  is too complicated to be attributed to a  $\sigma$ -bonded structure.<sup>6</sup> This, however, is not the case. The highest symmetry which can be postulated for the molecule as a whole is  $C_{2v}$  (a cisoid structure) or  $C_{2h}$  (a transoid structure). In the former, one would expect 44 infrared-active and 57 Raman-active vibrations,

while in the latter case there are 26 infrared-active and 31 Raman-active vibrations. For any lower symmetry, all 57 bands would be both infrared and Raman active. Even neglecting the possibility of coupling between the vibrations of the two rings, which seems to be the case, the vibrational spectrum should be quite complex. If we neglect the interaction between the two cyclopentadienyl rings and adopt the model,  $(C_5H_5)_2Hg$ , the symmetry is  $C_8$  and 27 vibrations are still active both in the infrared and the Raman spectra. In addition, the ring-Hg-ring skeletal vibrations may appear. In either case, the spectrum is expected to be quite complex, even neglecting possible combination and overtone bands.

It has been found that the infrared spectrum of  $(C_5H_5)_2Hg$  is essentially identical with that of  $(C_5H_5)HgCl$  above 400  $cm^{-1}$  (Table I). Furthermore, the spectrum of the latter is almost the same as those of  $(C_5H_5)HgBr$  and  $(C_5H_5)HgI$  above 400  $cm^{-1}$ . These results clearly indicate the lack of vibrational couplings between the internal vibrations of the two  $C_5H_5$  rings in  $(C_5H_5)_2Hg$  and between the  $C_5H_5$  ring and the halogen in the series of halogeno compounds mentioned above. In the following analysis, the simple  $(C_5H_5)Hg$  model will be used to discuss the ring vibrations, and a triatomic  $XY_2$  model ( $X$  = mercury atom;  $Y$  = a single atom having the mass of the  $C_5H_5$  ring), to discuss the skeletal vibrations.

### Ring Vibrations

In discussing the assignment of the vibrational spectrum of  $(C_5H_5)_2Hg$ , a comparison will be made with the spectrum of  $C_5H_6$ , for which the assignment has recently been made.<sup>11,12</sup> Five CH stretching vibrations are expected for the  $(C_5H_5)Hg$  model though six are present in  $C_5H_6$ . The frequencies of these vibrations correspond very closely to those of  $C_5H_6$ ; in  $(C_5H_5)_2Hg$  they appear at 3090, 3088, 3076, 3040, and 2970  $cm^{-1}$ , while in  $C_5H_6$  they appear at 3105, 3091, 3075, 3043, 2900, and 2886  $cm^{-1}$ . Two  $C=C$  stretching vibrations are expected for the  $(C_5H_5)Hg$  model, although only one band corresponding to this vibration is observed at 1530  $cm^{-1}$ . This was also the case in the infrared spectrum of  $C_5H_6$ . The  $C=C$  stretching bands are relatively weak in intensity. On going to lower frequencies, two CH bending vibrations are found at 1427 and 1383  $cm^{-1}$ , corresponding to those at 1441 and 1365  $cm^{-1}$  in  $C_5H_6$ . Two bands at 1296 and 1234  $cm^{-1}$  of  $(C_5H_5)_2Hg$  are assigned to CH bendings coupled with ring deformations; they correspond to the bands at 1292 and 1239  $cm^{-1}$  of  $C_5H_6$ . A band at 1109  $cm^{-1}$  of  $(C_5H_5)_2Hg$  may correspond to a ring deformation at 1106  $cm^{-1}$  of  $C_5H_6$ . The  $C_5H_6$  molecule exhibits the scissoring, rocking, twisting, and wagging vibrations characteristic of the  $CH_2$  group. In  $(C_5H_5)_2Hg$ , one of these hydrogens is replaced by a mercury atom. Thus the vibrations corresponding to these modes are now  $C(5)-H$  and  $C-Hg$  bending modes. Since the  $C-Hg$  bending modes are expected to be of extremely low frequency, two bands

(11) E. Gallinella, B. Fortunato, and P. Mirone, *J. Mol. Spectry.*, **24**, 345 (1967).

(12) H. P. Fritz and L. Schäfer, *Spectrochim. Acta*, **21**, 211 (1965).

TABLE I  
 VIBRATIONAL FREQUENCIES OF  $(C_5H_5)_2Hg$ ,  $C_5H_6$ , AND  $(C_5H_5)HgX$  TYPES OF COMPOUNDS IN SOLUTION ( $cm^{-1}$ )

Raman <sup>a</sup>	$(C_5H_5)_2Hg$		$C_5H_5HgCl$	$C_5H_5HgBr$	$C_5H_5HgI$	$C_5H_6$	Assignment <sup>d</sup>
	Ir <sup>b</sup>	Ir <sup>c</sup>	Ir <sup>c</sup>	Ir <sup>c</sup>	Ir <sup>c</sup>	Ir <sup>c</sup>	
	3090 s <sup>i</sup>	3105 m	3105 s	3105 s	3110 s	3105 m	$\nu$ (CH)
	3088 s	3098 m	3098 m	3090 s	3075 s	3091 s	$\nu$ (CH)
	3076 sh	3072 s	3072 s	3063 s	3060 sh	3075 m	$\nu$ (CH)
	3040 sh	3040 w	3040 w	3030 sh	3040 sh	3043 m	$\nu$ (CH)
	2970 w	2950 w	2950 w	2960 w	2960 w		$\nu$ (CH)
		1830 w	1830 w	1825 w	1821 w		Combination?
		1808	1810 w	1810 w	1808 w		Overtone?
		1630 w		1631 m	1635 w		Combination?
1530 w	1530 w	1543 w <sup>g</sup>	1540 w <sup>g</sup>	1540 w <sup>g</sup>	1540 w <sup>g</sup>	1501 w	$\nu$ (C=C)
1445 m							
1420 m	1427 m	1461 m <sup>g</sup>	1460 m <sup>g</sup>	1457 m <sup>g</sup>	1441 w		$\delta$ (CH)
1384 m	1383 m	1379 m	1378 m	1379 m	1365 vs		$\delta$ (CH)
1300 w	1296 m	1290 m	1289 m	1293 m	1292 m		$\delta$ (CH) + ring def
1230 w	1234 m	1228 m	1224 w	1230 w	1239 m		$\delta$ (CH) + ring def
1109 m	1109 m	1108 w	1110 vw	1110 vw	1106 w		Ring def
1080 w	1084 m	1089 m	1086 m	1086 m	1089 m		$\delta$ (CH)
1033 w	1026 m	1026 m	1019 m	1022 m			$\delta$ (CC(5)H)
985 w	988 m	990 m	989 s	988 s			$\delta$ (CC(5)H)
955 w	957 m	962 m	958 m	952 m	959 s		Ring def + $\delta$ (CH)
905 w	907 vs	941 s	938 vs	925 vs	925 sh		$\delta$ (CH)
874 s	885 vs	902 s	901 s	898 s	920 s		Ring def
		885 w	887 w				
815 s	822 m	819 m	818 s	820 s	805 m		Ring def
<i>f</i>	748 vs	756 vs	753 vs	750 vs	700 vw		$\pi$ (CH)
<i>f</i>	720 w	720 w	718 w	718 w			Combination?
639 s	646 s	653 s	650 s	643 s	664 vs		$\delta$ (CH)
<i>f</i>	575 w	565 w	564 w	566 w	515 w		Ring def
	348 s	359 s	342 s	336 s	...		Asym $\nu$ (Hg-C(5))
321 s	...	...	...	...	...		Sym $\nu$ (Hg-C(5))
	...	...	...	...	...		Sym $\nu$ (Hg-C(5))
	...	315 s	...	...	...		$\nu$ (Hg-Cl)
	...	...	232 s	...	...		$\nu$ (Hg-Br)
	200 m	197 m	220 m	220 m	...		$\delta$ (CC(5)Hg)
	...	...	...	186 s	...		$\nu$ (Hg-I)
	100 w	108 w	53 w	51 w	...		$\delta$ (C(5)HgX) <sup>h</sup>
	38 w						

<sup>a</sup> Carbon tetrachloride as the solvent. <sup>b</sup> Carbon disulfide and chloroform as the solvents. <sup>c</sup> Carbon disulfide as the solvent. <sup>d</sup> The assignments between 4000 and 500  $cm^{-1}$  are those given for  $C_5H_6$  in ref 11 and 12. The spectrum given for  $C_5H_6$  is taken from ref 11. <sup>e</sup>  $\nu$ , stretching;  $\delta$ , in-plane bending;  $\pi$ , out-of-plane bending. <sup>f</sup> These bands are hidden by the solvent band. <sup>g</sup> These values are taken from the perfluorocarbon spectrum of the compound. <sup>h</sup> X = C, Cl, Br, or I. <sup>i</sup> Intensity designations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

near 1000  $cm^{-1}$  (1026 and 988  $cm^{-1}$ ) have been assigned to the C(5)-H bending modes of  $(C_5H_5)_2Hg$ .

The vibrational spectrum of  $(C_5H_5)_2Hg$  is also similar to that of  $C_5H_6$  in the region from 1000 to 350  $cm^{-1}$ . As is shown in Table I,  $C_5H_6$  exhibits six ring vibrations in this region, and the corresponding vibrations are found for  $(C_5H_5)_2Hg$  at similar frequencies. The same is true for the in-plane and out-of-plane bendings of the aromatic CH groups.

#### Skeletal Vibrations

Thus far, the vibrations due to the  $C_5H_5$  ring have been discussed. The remaining bands arise from the ring-Hg-ring skeleton. The strong infrared band at 345  $cm^{-1}$  is assigned to the antisymmetric Hg-C stretching mode of the linear (or almost linear) C-Hg-C

bond. This frequency is much lower than the Hg-C stretching frequencies reported for other organomercury compounds (*ca.* 550  $cm^{-1}$ ).<sup>13,14</sup> Also, this band could be assigned to the ring deformation corresponding to the 350- $cm^{-1}$  band of  $C_5H_6$ . Nevertheless, it was assigned to the antisymmetric Hg-C stretching vibration of  $(C_5H_5)_2Hg$  because of the following reasons.

(1) In  $(C_5H_5)_2Hg$ , this band is relatively intense in the infrared spectrum, while there is also a very intense band in the Raman spectrum at 321  $cm^{-1}$ . Although  $C_5H_6$  exhibits a strong infrared band at 350  $cm^{-1}$ , this band is much weaker in the Raman spectrum. In studying the infrared spectra of a series of dialkylmer-

(13) D. Seybold and K. Dehnicke, *J. Organometal. Chem.* (Amsterdam), **11**, 1 (1968).

(14) J. H. S. Green, *Spectrochim. Acta*, **24A**, 863 (1968).

TABLE II  
 FAR-INFRARED SPECTRA OF  $(C_5H_5)_2Hg$  AND  $(C_5H_5)HgX$  TYPES OF COMPOUNDS ( $cm^{-1}$ )

		$\nu(Hg-C)$	$\nu(Hg-X)$	$\delta(CH_2)$	$\delta(CH_2X)$ or $\delta(CH_2C)$
$C_5H_5HgCl$	solid	345	292	200	90
	soln <sup>a</sup>	359	315	197	108
$C_5H_5HgBr$	solid	333, 340	214	200	64
	soln	342	232	220	53
$C_5H_5HgI$	solid	331	175	200	63
	soln	336	186	220	51
$(C_5H_5)_2Hg$	solid	345	...	200	100
	soln	348	...	200	100

<sup>a</sup> The solvent used in all solution spectra was carbon disulfide.

cury compounds, Seybold and Dehnicke<sup>13</sup> have observed that in some cases (for example diethylmercury and diisopropylmercury), the symmetric stretching vibration appears strongly only in the Raman spectrum and the asymmetric stretching vibration is observed strongly only in the infrared spectrum.

(2) Since this band does not appear in the same position in the infrared and Raman spectra of  $(C_5H_5)_2Hg$ , it appears that two different vibrations are observed. They are separated by  $24\text{ cm}^{-1}$ , with the antisymmetric vibration appearing higher than the symmetric vibration. In the case of  $C_5H_8$ , however, the band appeared at  $350\text{ cm}^{-1}$  in both the infrared and Raman spectra.<sup>11</sup>

(3) In the infrared spectra of other compounds containing a  $\sigma$ -bonded cyclopentadienyl ring, namely,  $(C_5H_5)Si(CH_3)_3$  and  $(\pi-C_5H_5)Fe(CO)_2(\sigma-C_5H_5)$ , no strong bands were observed in this region. A weak band, however, is observed in the solid state at  $370\text{ cm}^{-1}$  corresponding to the  $375\text{-cm}^{-1}$  band of  $(C_5H_5)_2Hg$ .

(4) If it is assumed that the  $C_5H_5$  rings are single atoms and a simple calculation on a linear  $XY_2$  model is performed, a Urey-Bradley stretching force constant of  $2.76\text{ m dyn/\AA}$  is obtained as compared to the value of  $2.32\text{ m dyn/\AA}$  found for dimethylmercury. These two values are relatively close in view of the approximations made in these calculations.

(5) According to Table II, both  $(C_5H_5)_2Hg$  and  $(C_5H_5)HgCl$  exhibit the Hg-C stretching mode at  $345\text{ cm}^{-1}$ . Similarly, both  $(CH_3)_2Hg$  and  $(CH_3)HgCl$  exhibit the Hg-C stretching at  $550\text{ cm}^{-1}$ . This band shifts to  $546\text{ cm}^{-1}$  in  $(CH_3)HgBr$  and to  $535\text{ cm}^{-1}$  in  $(CH_3)HgI$ .<sup>15</sup> Similarly, the  $345\text{-cm}^{-1}$  band of  $(C_5H_5)HgCl$  shifts to  $333$  and  $340\text{ cm}^{-1}$  in  $(C_5H_5)HgBr$  and to  $331\text{ cm}^{-1}$  in  $(C_5H_5)HgI$ .

The fact that  $(C_5H_5)_2Hg$  exhibits only one Hg-C stretching band in the infrared spectrum strongly suggests that the C-Hg-C bond is linear, both in the solid state and in solution. However, the C-Hg-C bonds in some organomercury compounds are reported to be bent in solution.<sup>16</sup> It is rather difficult, however, to detect a small deviation from linear structure by vibrational spectroscopy. Therefore, a bent structure involving the C-Hg-C angle of  $150\text{--}170^\circ$  cannot be excluded from our consideration.

In addition to the Hg-C stretching bands, a series of

compounds of the type  $(C_5H_5)HgX$  ( $X = \text{halogen}$ ) exhibit the Hg-X stretching band. The Hg-Cl and Hg-Br stretching bands have been assigned to the regions  $330\text{--}310$  and  $250\text{--}200\text{ cm}^{-1}$ , respectively, for the  $RHgCl$  type of compounds where R is an alkyl group.<sup>17</sup> In agreement with these group frequencies,  $(C_5H_5)HgCl$  and  $(C_5H_5)HgBr$  exhibit their Hg-X stretching frequencies at  $292$  and  $214\text{ cm}^{-1}$ , respectively, in the solid state. The Hg-I stretching frequency of  $CH_3HgI$  is reported to be  $181\text{ cm}^{-1}$ .<sup>14</sup> The corresponding band is found at  $175\text{ cm}^{-1}$  for  $(C_5H_5)HgI$  in the solid state.

As mentioned earlier, two C-Hg bending modes are expected to appear in the low-frequency region. The band at  $297\text{ cm}^{-1}$  of  $(C_2H_5)_2HgBr$ <sup>14</sup> and the band at  $210\text{ cm}^{-1}$  of  $(C_6H_5)_2Hg$ <sup>12</sup> have been assigned to these bending modes. A broad band at *ca.*  $200\text{ cm}^{-1}$  was observed for all of the compounds containing the  $(C_5H_5)Hg$  group. Therefore, this broad band was assigned to the C-Hg bending modes. Another bending mode involving the change in the C-Hg-C angle is reported to be at  $156\text{ cm}^{-1}$  in  $(CH_3)_2Hg$ <sup>18</sup> and at  $98\text{ cm}^{-1}$  in  $(C_6H_5)_2Hg$ .<sup>13</sup> The corresponding band is found at  $100\text{ cm}^{-1}$  in  $(C_5H_5)_2Hg$ . The C-Hg-X bending mode appears between  $100$  and  $50\text{ cm}^{-1}$  in the series of compounds of the type  $(C_6H_5)HgX$ .<sup>14</sup> The corresponding bands of the  $(C_5H_5)HgX$ -type compounds are at  $90\text{ cm}^{-1}$  for  $X = Cl$ ,  $64\text{ cm}^{-1}$  for  $X = Br$ , and  $63\text{ cm}^{-1}$  for  $X = I$ . Finally,  $(C_5H_5)_2Hg$  is expected to show a twisting mode of the two rings, relative to each other. A band at  $38\text{ cm}^{-1}$  observed for this compound may be due to this mode.

As stated previously, it is rather difficult to determine the relative orientation of two cyclopentadienyl rings from vibrational spectroscopy owing to the lack of vibrational couplings between two rings. However, the dipole moment of  $(C_5H_5)_2Hg$  in a benzene solution is reported to be  $1.0\text{ D}$ .<sup>19</sup> Hence, the transoid structure having a center of symmetry can be excluded from our consideration.

There are several nontransoid structures which may account for the observed dipole moment. One of them is the cisoid structure of  $C_{2v}$  symmetry shown in Figure 4. The other is an intermediate structure between the cisoid and the transoid structures. In solution, an equilibrium may exist between these forms. An even more likely structure may involve free rotation of the

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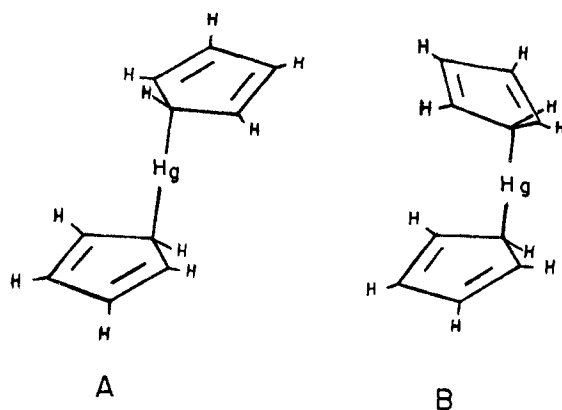


Figure 4.—The two extreme orientations of the  $C_5H_5$  rings with respect to each other: transoid structure (A) and cisoid structure (B).

cyclopentadienyl rings about the C–Hg–C axis. Complete determination of the structure is difficult to make unless theoretical values of the dipole moment are calculated for each structure.

### The Pmr Spectrum

As stated in the Introduction, the pmr spectrum of  $(C_5H_5)_2Hg$  has been controversial. If the theory of valence tautomerism proposed by Piper and Wilkinson<sup>5</sup> is correct, the low-temperature pmr spectrum of  $(C_5H_5)_2Hg$  should exhibit three peaks, with the expected intensity ratio of 2:2:1. Previously, Dvoryantseva, *et al.*,<sup>20</sup> measured the pmr spectrum of this compound

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in a tetrahydrofuran solution at  $-70^\circ$ . Contrary to the expectation from valence tautomerism, they observed only a single peak at  $-70^\circ$ . In order to confirm their results, the pmr spectrum of  $(C_5H_5)_2Hg$  was measured in various solvents down to  $-70^\circ$ . In triethylamine, only a single peak was observed. In  $CS_2$ , the peak was noticeably broadened as the temperature reached  $-70^\circ$ . In  $SO_2$  solution, however, three distinct peaks were observed.<sup>21</sup> These results have recently been questioned by Nesmeyanov, *et al.*,<sup>22</sup> who observed no splitting of the  $(C_5H_5)_2Hg$  signal at  $-70^\circ$ , using sulfur dioxide as the solvent. We are now carrying out a more careful study to confirm our results. Even admitting the correctness of their results, however, it is dangerous to draw the conclusion that there is no valence tautomerism on the basis of this negative evidence. The low-temperature pmr spectrum of  $(C_5H_5)HgCl$  has also been studied, in the hope of observing a splitting at low temperatures. Tetrahydrofuran, diethyl ether, and sulfur dioxide were used as the solvents and the temperature was lowered to  $-70^\circ$ . However, no change was observed in the pattern of the spectrum. The reason for this failure cannot be understood until a more elaborate theory is developed about the mechanism of valence tautomerism and the solvent effect on it.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF YORK, YORK, ENGLAND

## Raman Spectroscopic Studies of the Structure of the Lower Chlorides of Indium in the Molten State

By J. H. R. CLARKE AND R. E. HESTER<sup>1</sup>

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Raman spectra have been obtained over a range of temperatures for molten and solid  $InCl_2$ , molten and solid  $In_2Cl_3$ , and  $InCl$  dissolved in the molten  $LiCl$ – $KCl$  eutectic. It is shown that  $InCl_2$  has the constitution  $In^+InCl_4^-$  in the liquid and probably also in the solid state. The spectra of molten  $In_2Cl_3$  and molten  $InCl \cdot 4(Li,K)Cl$  both show the presence of  $In(III)$  chloro complexes and it is concluded that there is disproportionation of  $In^+$  in the presence of free chloride and that  $In^0$  coordinates with  $In^{III}Cl_4^-$  to form metal–metal bonds. A strong, polarized Raman band at *ca.*  $170\text{ cm}^{-1}$  is assigned to an  $In$ – $In$  stretching mode.

### Introduction

In addition to indium monochloride and trichloride a number of intermediate compounds have been characterized for the indium–chlorine system in the solid state.<sup>2–5</sup> The existence of  $InCl_2$  as a definite compound

was at one time called into doubt,<sup>2</sup> but careful reinvestigation<sup>4</sup> of the phase diagram has confirmed its existence in the solid state. The compound is diamagnetic<sup>6</sup> and it has been suggested<sup>7</sup> that it might consist of  $InCl_2$  dimers, although the alternative mixed-valence structure  $In^IIn^{III}Cl_4$  seems more likely by analogy with the

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