

measurements indicate that the $\alpha_{\text{H}_2\text{O}}$ is not particularly small, being approximately 0.2 of that in pure water.²⁷ In our experiments it was found that the base catalyzed parahydrogen conversion was very slow, barely exceeding that to be expected for the nuclear moments of the protons in the solvent and certainly not greater than that found in 0.1 *M* aqueous alkali. These data show that the

(27) J. G. Burtle, *J. Phys. Chem.*, **44**, 1675 (1952).

ratio $\gamma_{\text{OH}}\text{-}\gamma_{\text{H}_2\text{O}}/\gamma_{\text{H}}\text{-}\alpha_{\text{H}_2\text{O}}$ is not a large quantity in the amine solvents. The result is readily understandable if $\gamma_{\text{OH}}\text{-}/\gamma_{\text{H}}\text{-}$ is approximately one, as it is in aqueous alkali, since $\gamma_{\text{H}}\text{-}$ cannot be very large, the solubility of hydrogen being not unlike that in pure water. By contrast, for the ratio $\gamma_{\text{HB}}\gamma_{\text{OH}}\text{-}/\gamma_{\text{B}}\text{-}\alpha_{\text{H}_2\text{O}}$ to reach so extreme a value in the indicator studies, it is very likely that the ratio $\gamma_{\text{OH}}\text{-}/\gamma_{\text{B}}\text{-}$ is a very large number and is responsible for much of the apparent basicity of the medium.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND, COLLEGE PARK, MARYLAND]

The Vibrational Spectra and Structure of Bis-cyclopentadienylmagnesium

BY ELLIS R. LIPPINCOTT, J. XAVIER¹ AND D. STEELE¹

RECEIVED NOVEMBER 30, 1960

A study of the infrared and Raman spectra of bis-cyclopentadienylmagnesium in solution and in the solid state is reported. A comparison of the observed vibrational frequencies with those obtained for ferrocene indicate that the molecular geometry is best represented by a "sandwich" structure. An assignment of frequencies has been made which is quite similar to that reported for ferrocene and related compounds. The results are not in agreement with the early reports of an essentially ionic bonding in bis-cyclopentadienylmagnesium and are better explained by the presence of covalent ring-to-metal bonding, which is weaker than the metal to ring bonding in ferrocene.

Introduction

The discovery of ferrocene has led to the synthesis and characterization of a large number of organo-metallic compounds.²⁻⁴ Physicochemical investigations have reasonably well established the molecular structure and the type of chemical bonding in most of these substances. However, there still exist some doubts regarding the nature of the bonding in metal cyclopentadienyls and their derivatives.

A pentagonal antiprismatic structural configuration has been assigned to ferrocene and similar cyclopentadienyls. Weiss and Fischer⁵ have shown that in the crystal form $\text{Mg}(\text{C}_5\text{H}_5)_2$ has a "sandwich" configuration and proposed a rather weak covalent d^2sp^3 hybridization overlapping the ionic electrostatic binding between the metal and cyclopentadienyl ions. However, based on magnetic, spectral and chemical investigations, Wilkinson, *et al.*,⁶ conclude that the bonding in bis-cyclopentadienyl $\text{Mg}(\text{II})$ and $\text{Mn}(\text{II})$ is essentially ionic. According to these authors, two cyclopentadienide anions are expected on electrostatic grounds to align themselves on opposite sides of the cation with their planes parallel, the structure thus very closely resembling that of "sandwich bonded" molecules, such as ferrocene. The configuration in the case of the ionic molecules (*e.g.*, $\text{Mn}(\text{C}_5\text{H}_5)_2$ or $\text{Mg}(\text{C}_5\text{H}_5)_2$) is thus assumed to be due merely to the geometry resulting from charge distribution, whereas in the case of ferrocene-like

molecules, it is a requirement of the metal-to-ring covalent bonding. This postulation of difference in bond type has been prompted by notable differences in chemical properties, by conductivity measurements in liquid ammonia⁵ and by mass spectra measurements and determination of appearance potentials.⁷ The mass spectra do not provide confirmative evidence regarding the configuration. However, the stability of the parent compound is indicated by the stability of molecule-ions in the mass spectra. In the case of Mg and Mn cyclopentadienides, the parent molecule-ions $\text{C}_{10}\text{H}_{10}\text{M}^+$ are relatively unstable, contributing only 20% to the total ion yield in contrast to the Fe , Co , Cr , etc., compounds, in which the molecule-ion contributes roughly 50% or more of the total ion yield. The instability of the molecule-ions in Mg and Mn compounds again is evidenced by the enhanced yields of $\text{C}_5\text{H}_5\text{M}^+$ and M^+ ions. These observations, along with the chemical properties of the compounds, such as metathetical reactions with ferrous chloride to form ferrocene, hydrolysis with water, etc., have led the previous workers⁵⁻⁷ to reach the conclusion that the metal-to-ring bond in Mn and Mg cyclopentadienyls is of a quite different nature from that of the bonding in ferrocene-type molecules.

The concept of ionic bonding in $\text{Mg}(\text{C}_5\text{H}_5)_2$ has been discussed by Cotton and Reynolds.⁸ The analogy between the spectrum of $\text{Mg}(\text{C}_5\text{H}_5)_2$, especially in the C-H stretching region, and those of ferrocene and nickelocene indicate the sandwich structure in the free state. The existence of the ionic bonding in the magnesium compound has then been evaluated from a consideration of the molecular orbital overlap and on the basis of ionization potentials. Finally, they conclude that the magnesium compound does behave as though

(1) Post-doctoral Research Fellows.

(2) (a) M. Rausch, M. Vogel and H. Rosenberg, *J. Chem. Ed.*, **34**, 268 (1957); (b) E. O. Fischer, *Angew. Chem.*, **475** (1955).

(3) P. L. Pauson, *Quart. Rev. (London)*, **9**, No. 4, 391 (1955).

(4) "Advances in Inorganic Chemistry and Radiochemistry," Editors, H. J. Emeleus and A. G. Sharp, Vol. I, Academic Press, Inc., New York, N. Y., 1959, p. 55.

(5) E. Weiss and E. O. Fischer, *Z. anorg. u. allgem. Chem.*, **278**, 219 (1955); E. O. Fischer and S. Schreiner, *Ber.*, **92**, 938 (1959).

(6) G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. Nuclear Chem.*, **2**, 95 (1956).

(7) L. Friedman, A. P. Irsa and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955).

(8) F. A. Cotton and L. T. Reynolds, *ibid.*, **80**, 269 (1958).

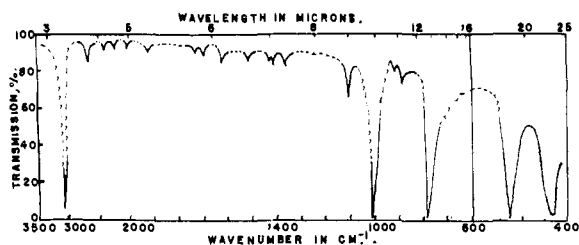


Fig. 1.—Infrared spectrum of $\text{Mg}(\text{C}_5\text{H}_5)_2$ in benzene solution; concentration, approximately 1 M .

the net charge separation is appreciable, this leading to a tendency toward ionic dissociation.

The metal-to-ring bond energies calculated by subtracting ionization potentials of the free metal atom from the appearance potential of the corresponding ion from $(\text{C}_5\text{H}_5)_2\text{M}$ also indicate weaker bonding in $\text{Mg}(\text{C}_5\text{H}_5)_2$ and $\text{Mn}(\text{C}_5\text{H}_5)_2$.⁷

The structure of the so-called "ionic" metal-cyclopentadienyls thus seems to be an interesting problem. The present work was undertaken with the idea of gaining a better insight into the nature of the bonding between the metal and the cyclopentadienyl ring in $\text{Mg}(\text{C}_5\text{H}_5)_2$.

Experimental

Bis-cyclopentadienylmagnesium was prepared according to the method of Wilkinson, *et al.*⁶ The cyclopentadienylmagnesium bromide was decomposed in vacuum ($\sim 10^{-4}$ mm.) and the sublimate led through a glass-wool plug into a tube into which the solvent was later distilled. The apparatus was designed primarily to exclude air and moisture which would instantaneously decompose the product. By this method, the compound could be purified by a multiple sublimation process. The purity of the sample was established by melting point determination in a sealed tube (observed 176–179°) and also by the colorless solution obtained in benzene or cyclohexane. The final transfer of the solution to the Raman tube was cautiously made after sealing the ends and allowing the solution to flow slowly into the Raman tube, avoiding the transference of solid particles along with the solution. A near saturated solution (at room temperature) was thus sealed into the Raman tube. Benzene and cyclohexane were employed as solvents, the solubility being greater in the former solvent. The solvents were degassed before placing them in the tube containing the cyclopentadienylmagnesium.

Raman spectra were obtained by using a two-prism Huet spectrograph (aperture F/8) with a dispersion of 18 Å./mm. at 4358 Å. Excitation with both 4358 and 5461 Å. Hg was accomplished with a low pressure, water-cooled Toronto arc, using filters and photographic plates described earlier.⁹ Infrared spectra were run on a Beckman IR4 automatic recording spectrophotometer. Cells of thickness 0.004 and 0.015 cm. were used for solutions, the openings having been sealed tightly with Teflon plugs and "Bi-Seal" self-bonding electrical tape (Bishop Manufacturing Corp. Cedar Grove, N.Y.) after insertion of the solutions. Spectra in the region 400–800 cm^{-1} were studied with the same solutions using AgCl cells. The infrared spectra of the solid compound were taken using a diamond cell.¹⁰ The cell was loaded inside a dry box containing an inert atmosphere. Medium pressure was applied between the diamonds. It was found that little decomposition occurred during the time of running of the spectra, as no appreciable change was observed in several consecutive spectra taken over a period of 2 to 3 hr.

The infrared spectra are reproduced in Figs. 1–3. The vibrational spectrum of cyclopentadienylmagnesium is

(9) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).

(10) C. E. Weir, E. R. Lippincott, A. Van Valkenberg and E. N. Bunting, *J. Research Natl. Bur. Standards*, **A63**, 55 (1959); E. R. Lippincott, C. E. Weir and F. E. Welsh, *Anal. Chem.* (accepted for publication).

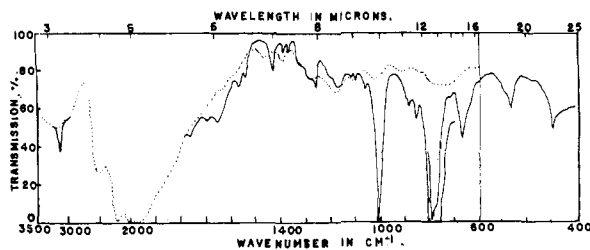


Fig. 2.———, infrared spectrum of $\text{Mg}(\text{C}_5\text{H}_5)_2$ in solid state using diamond cell; , spectrum of diamond cell.

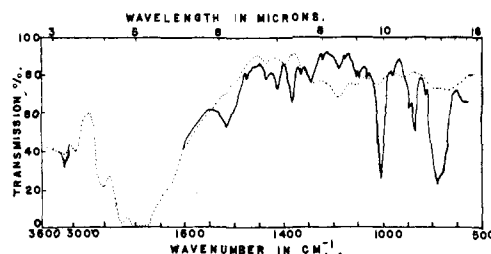


Fig. 3.———, infrared spectrum of $\text{Mn}(\text{C}_5\text{H}_5)_2$ in solid state using diamond cell; , spectrum of diamond cell.

listed in Table I, along with those of ferrocene and ruthenocene for comparison. The infrared spectra of cyclopentadienylmagnesium and -manganese in the solid state are given in Table II.

TABLE I

THE VIBRATIONAL SPECTRA OF $\text{Mg}(\text{C}_5\text{H}_5)_2$, $\text{Fe}(\text{C}_5\text{H}_5)_2^a$ AND $\text{Ru}(\text{C}_5\text{H}_5)_2^a$

$\text{Mg}(\text{C}_5\text{H}_5)_2$		$\text{Fe}(\text{C}_5\text{H}_5)_2$		$\text{Ru}(\text{C}_5\text{H}_5)_2$	
Raman	Infrared (in solution)	Raman	Infrared	Raman	Infrared
191ms			170m		
229w		303m		330s	
		388w		402m	
	440ms		478s		446s
	526ms		492s		528w
752vw	783s		782w		763w
806vww	890vw		811s	804w	806s
	915vww		834w		835w
(1000)	1008s	1010w	1002s	996m	1002s
		1050w	1051w	1056m	1050m
1109ms	1108m	1105s	1108s	1112s	1104s
1163ms		1178m	1188w	1193w	
	1344vww	1363vw	1356w		1360w
1410vww	1420w	1408vw	1411s	1412m	1413m
	1425vw				
	1516vww	1566vw			
	1610m				
	1625vw		1620m		1622m
			1650m		1651m
			1684m		1684m
	1700vww		1720m		1727m
	1736vww		1758m		1774m
	1928vww				
	2050vww				
	2395vww				
(3080)	2600vww	3085m		3089m	
3104s	3080s	3099s	3085s	3104s	3100m

^a From ref. 9. s = strong; m = medium; w = weak; v = very.

The crystal spectra obtained using the diamond cell are in fairly good agreement with those run by the KBr disc

TABLE II
INFRARED SPECTRA OF $Mg(C_6H_6)_2$ AND $Mn(C_6H_6)_2$ IN SOLID STATE

KBr disc ^a	$Mg(C_6H_6)_2$ Single crystal ^b	Diamond pressure cell	$Mn(C_6H_6)_2$
441m		442m	
524m		527m	
663m		668m	
	700s		
758s	760s	764ms	748w
			765w
779vw		780s	780s
891		858w	830vw
		886vw	868ms
913			
959			960w
1004s	980ms	1008s	1008s
	1020w		1045vww
1058		1060vww	1062vw
1108	1100w	1106w	1095w
			1110w
		1176w	1158vw
			1176vw
1257	1250ms	1260w	1240w
1364	1345m	1368vw	1364m
	1395vw		
1428m	1430ms	1434m	1426m
	1480vw		1466w
1516	1540m	1540vw	1545vw
		1570vw	
1629	1605vw	1652vw	1634m
	1675vww	1700vww	
1751	1740w		
	1860vww		
	1960vw		
2050	2070ms		
	2200ms		
(2249)	2270ms		
	2330vww		
2373	2390vw		
	2460vw		
	2610vw		
2658	2640w		
	2730vw		
	2840vww		
2913	3000w		
3063m	3060s	3100ms	3106ms
	3145w		

^a From ref. 11. ^b From ref. 6 (approximate readings from the figure).

technique¹¹ as well as those obtained in solutions (Tables I and II). The deviation of the frequencies and intensities from those obtained by Wilkinson, *et al.*,⁶ for a single-crystal spectrum is due to the interference of decomposition products. The spectra of bis-cyclopentadienylmagnesium (and manganese) run at long intervals of time using the diamond cell, also showed such deviations of frequencies and intensities, which were similar to those obtained by Wilkinson, *et al.*, on single-crystal spectra. The bis-cyclopentadienylmanganese(II) decomposed much more easily in the diamond cells than the corresponding magnesium compound. The increase in absorption intensities of bands at about 1008, 1106 and 1420 cm^{-1} during decomposition of the original compounds is observed readily and leaves little doubt that the spectrum reported for the single crystal contains large amounts of decomposed products.

Assignment of Frequencies.—A detailed account of the vibrational spectra of ferrocene, ruthenocene and nickelocene has been given by Lippincott and Nelson.⁹ The fre-

TABLE III
FREQUENCY ASSIGNMENTS (FUNDAMENTAL MODES OF VIBRATION)^a

Species	Frequency	$Mg(C_6H_6)_2$	Description
A_{1g} (Raman)	1	3104	Sym. CH stretching
	2	806	Sym. CH bending (\perp)
	3	1109	Sym. ring breathing
	4	191	Sym. ring metal stretching
A_{1u} (inactive)	5	(1250) ^b	CH bending (\parallel)
	6	...	Internal rotation
A_{2g} (inactive)	7	(1200)	CH bending
A_{2u} (infrared)	8	3080	CH stretching
	9	783	CH bending
	10	1108	Antisym. ring breathing
	11	526	Antisym. ring metal stretching
E_{1g} (Raman)	12	(3085)	CH stretching
	13	(990)	CH bending (\parallel)
	14	806	CH bending (\perp)
	15	1410	Sym. C-C stretch
	16	229	Sym. ring tilt
		(186 calcd.)	
E_{1u} (infrared)	17	(3100)	CH stretching
	18	1008	CH bending (\parallel)
	19	886 ^b	CH bending (\perp)
	20	1420	Antisym. C-C stretching
	21	440	Antisym. ring tilt
	22	107	Ring metal ring bending
		(calcd.)	
E_{2g} (Raman)	23	(3085)	CH stretching
	24	1163	CH bending (\parallel)
	25	(1050)	CH bending (\perp)
	26	(1560)	C-C stretching
	27	(885)	Ring distortion (\parallel)
	28	(570)	Ring distortion (\perp)
E_{2u} (inactive)	29	(3100)	CH stretching
	30	(1170) ^b	CH bending
	31	(1050) ^b	CH bending (\perp)
	32	(1560) ^b	C-C stretch
	33	(885) ^b	Ring deformation
	34	(570)	Ring deformation

^a Assignments not observed, but made in comparison to ferrocene and nickelocene.⁹ ^b Observed in crystal spectra, using diamond cells.

quency assignments of the fundamental modes of vibration of $Mg(C_6H_6)_2$ resemble closely the results obtained for ferrocene.

Assignments of fundamental modes are as shown in Table III. It is found that the arguments put forward in making the assignments of fundamental modes of ferrocene hold quite satisfactorily for $Mg(C_6H_6)_2$. An attempt is also made here to explain the appearance of non-fundamental bands (Table IV).

The selection rules for a D_{6d} sandwich structure give A_{1g} , E_{1g} and E_{2g} as Raman active species and A_{2u} and E_{1u} as infrared active species. A_{1u} , A_{2g} and E_{2u} are inactive species. There are thus 15 Raman ($4A_{1g}$, $5E_{1g}$ and $6E_{2g}$) and 10 infrared ($4A_{2u}$ and $6E_{1u}$) fundamental vibrational frequencies predicted, though all are not observed. It is seen for ferrocene that certain fundamental modes of vibrations, which, on symmetry considerations, are forbidden in the infrared region, do appear in the spectrum of the solid.¹² This is also noticed in crystal spectra of $Mg(C_6H_6)_2$ (see Table II).

A comparison of the spectra of ferrocene and ruthenocene with that of $Mg(C_6H_6)_2$ reveals that the frequencies due to

(11) H. P. Fritz, *Chem. Ber.*, **92**, 780 (1959).

(12) W. K. Winter, B. Curnutte, Jr., and S. E. Whitecomb, *Spectrochim. Acta*, **12**, 1085 (1959).

TABLE IV
 ASSIGNMENT OF OBSERVED NON-FUNDAMENTAL FREQUENCIES

Frequency Raman	Explanation	Type
752	$\omega_4 + \omega_{23} = 191 + 570 = 761$	$A_{1g} \times E_{2g} = E_{2g}$
1345	$\omega_4 + \omega_{24} = 191 + 1163 = 1354$	$A_{1g} \times E_{2g} = E_{2g}$
Infrared		
1363	$\omega_{30} + \omega_4 = 1170 + 191 = 1361$	$E_{2u} \times A_{1g} = E_{2u}$
1425	$\omega_{16} + \omega_7 = 229 + 1200 = 1429$	$A_{2g} \times E_{1g} = E_{1g}$
	$\omega_{21} + \omega_{13} = 440 + 990 = 1430$	$E_{1u} \times E_{1g} = A_{1u} + A_{2u} + E_{2u}$
1516	$\omega_{13} + \omega_{11} = 990 + 526 = 1516$	$E_{1g} \times A_{2u} = E_{1u}$
	$\omega_{15} + \omega_{22} = 1410 + 107 = 1517$	$E_{1g} \times E_{1u} = A_{1u} + A_{2u} + E_{2u}$
1540	$\omega_{10} + \omega_{21} = 1108 + 440 = 1548$	$A_{2u} \times E_{1u} = E_{1g}$
	$\omega_3 + \omega_{21} = 1109 + 440 = 1549$	$A_{1g} \times E_{1u} = E_{1u}$
1570	$\omega_{18} + \omega_{25} = 1008 + 570 = 1578$	$E_{1u} \times E_{2g} = E_{1u} + E_{2u}$
	$\omega_{11} + \omega_{25} = 526 + 1050 = 1576$	$A_{2u} + E_{2g} = E_{2u}$
1610	$2 \times \omega_{14} = 2 \times 806 = 1612$	$2E_{1g} = A_{1g} + E_{2g}$
1625	$\omega_3 + \omega_{11} = 1109 + 526 = 1635$	$A_{1g} \times A_{2u} = A_{2u}$
1700	$\omega_7 + \omega_{11} = 1200 + 526 = 1726$	$A_{2g} \times A_{2u} = A_{1u}$
1736	$\omega_4 + \omega_{26} = 191 + 1560 = 1751$	$A_{1g} \times E_{2g} = E_{2g}$
1928	$\omega_{19} + \omega_{25} = 886 + 1050 = 1936$	$E_{1u} \times E_{2g} = E_{1u} + E_{2u}$
2050	$\omega_{18} + \omega_{25} = 1008 + 1050 = 2058$	$E_{1u} \times E_{2g} = E_{1u} + E_{2u}$
2395	$\omega_{13} + \omega_{20} = 990 + 1420 = 2410$	$E_{1g} \times E_{1u} = A_{1u} + A_{2u} + E_{2u}$
2600	$\omega_7 + \omega_{15} = 1200 + 1410 = 2610$	$A_{2g} \times E_{1g} = E_{1g}$

vibrations within the rings are essentially the same, while the ring-metal-ring vibrations occur at different positions. The symmetric stretching frequency in ferrocene is at 303 cm^{-1} , in ruthenocene at 330 cm^{-1} in nickelocene (calculated to be) at 200 cm^{-1} and in $\text{Mg}(\text{C}_5\text{H}_5)_2$ at 191 cm^{-1} . This would indicate a much weaker ring-metal bonding in $\text{Mg}(\text{C}_5\text{H}_5)_2$. A comparison of approximate force constants computed from this symmetric stretching mode indicates that the bond energy in $\text{Mg}(\text{C}_5\text{H}_5)_2$ would be about half of that in ferrocene. Since the bonding is appreciably weaker, the ring modes may be expected to resemble more closely those for a free C_5H_5 ring system. Consequently, some frequencies are expected to appear much more weakly in $\text{Mg}(\text{C}_5\text{H}_5)_2$ than the corresponding ones in ferrocene, etc., when they are forbidden by selection rules for a free C_5H_5 ring. This has been observed for the band at 1108 cm^{-1} , which is unusually weak in $\text{Mg}(\text{C}_5\text{H}_5)_2$.

It is known that some of the frequencies due to the linear XY_2 type modes are dependent on the mass of the metal atom and on the force constants. The assignment of the ring-metal antisymmetric stretching frequency of the magnesium compound has been made at 526 cm^{-1} . This is the position expected for this frequency, when allowance is made for the mass of the Mg atom, from the unambiguous assignment of the totally symmetric stretching frequency at 191 cm^{-1} . It should be noted that this particular band is at a higher frequency than the corresponding frequency in ferrocene, which is observed at 478 cm^{-1} .

Certain deviations in the position and intensity of the bands have been noticed in the spectra of $\text{Mg}(\text{C}_5\text{H}_5)_2$ and of ferrocene, though the two spectra fundamentally resemble each other. The frequency at 440 cm^{-1} in the spectra of $\text{Mg}(\text{C}_5\text{H}_5)_2$ is assigned to an antisymmetric ring tilt mode, while the corresponding value in ferrocene is 492 cm^{-1} . Both bands are quite intense. However, the low value of this mode in the magnesium compound can be explained on the basis of a weak bonding in the molecule compared to that in ferrocene.

Another striking difference between the spectra of $\text{Mg}(\text{C}_5\text{H}_5)_2$ and ferrocene is the low intensity of the 1420 cm^{-1} band in the former, in contrast to the strong one at 1411 cm^{-1} in ferrocene. It seems difficult to give a convincing explanation for this change in the intensity of the degenerate C-C stretching mode. However, it is observed that the intensity of the same band in the solid spectrum of $\text{Mg}(\text{C}_5\text{H}_5)_2$ compares favorably with that of ferrocene. A solvent effect of this particular band presumably lowers the intensity in solution spectra.

Considerable evidence for the covalent nature of the bonding in bis-cyclopentadienylmagnesium can be found by a consideration of the intensity of the absorption band at 526 cm^{-1} , the antisymmetric ring-metal stretching mode. The

absolute intensity A of an absorption band is given by the relation¹³

$$A = \frac{1}{Cl} \int \log_{10} \left(\frac{I_0}{I_\nu} \right) \nu d\nu = \frac{N\pi}{3c} g \left(\frac{\delta\mu}{3Q} \right)^2$$

For practical purposes¹⁴

$$A = \frac{\pi}{2} \times \frac{1}{Cl} \log_{10} \left(\frac{I_0}{I_\nu} \right) \nu \times \Delta\nu^{1/2}$$

where C = concentration of the solute in molecules per ml.

c = velocity of light

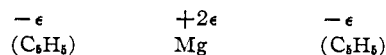
l = cell length in cm.

$I_0\nu$ and I_ν are incident and transmitted intensities of monochromatic radiation of frequency ν

$\Delta\nu^{1/2}$ = half-intensity width of the absorption band

g = degeneracy factor (= 1 in this case).

For the antisymmetric ring-metal stretching vibration it can be easily shown that $\delta\mu/\delta r = 2e$, assuming the ionic model



e is equal to the electronic charge if the compound is considered to be fully ionic.

Then $\delta\mu/\delta r = 9.604 \times 10^{-10}$ e.s.u. or 9.604 D./Å. Thus the absolute intensity on the theoretical basis should be $A = 194 \times 10^{-7}$ cm^{-2} molecules⁻¹ sec.⁻¹.

The observed intensity in molar benzene solution is found, using Ramsay's technique,¹⁴ to be approximately 2.9×10^{-7} . This is lower than the intensity obtained on the above theoretical basis by a factor of 68. This corresponds to a value of 1.6 D./Å. for $\delta\mu/\delta r$. This may be compared with the experimental value for the strongly polar C-F bond ranging from 5-6 D./Å. The predominantly covalent nature of the ring-metal bonding is, therefore, evidenced by the low observed absorption intensity, compared with the theoretical for a simple triatomic system.

In support of this it is found that the peak intensity at equivalent concentration and cell thickness for the 526 cm^{-1} antisymmetric ring-metal-ring stretching band in $\text{Mg}(\text{C}_5\text{H}_5)_2$ is equal to or slightly less than that for the peak intensity of the corresponding mode in ferrocene at 478 cm^{-1} . The argument holds equally well if the 492 cm^{-1} band in ferrocene is assigned to the antisymmetric ring-metal stretching mode. One would expect the peak intensity for the 526 cm^{-1} band in $\text{Mg}(\text{C}_5\text{H}_5)_2$ to be very much greater than that for the corresponding band in ferrocene, if the former molecule has appreciable ionic bonding.

(13) "Molecular Vibrations," E. B. Wilson, J. C. Decius and P. C. Cross, McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 163 ff.

(14) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

Discussion

As has been shown, the intensity of the antisymmetric stretching mode is inconsistent with predominantly ionic character. For an essentially ionic system the model used to evaluate the intensity of this mode will be good though likely to lead to a slight overestimate of the intensity due to coupling of the vibration with the cyclopentadienyl modes. Unfortunately the model cannot be used to determine the extent of the ionic character since with covalent bonding rehybridizations seriously modify the transition moment. Thus the C-F bond in fluorocarbons has a dipole moment of about 1.3 D., whereas intensity studies have shown that the stretching gradient $\delta\mu/\delta r_{CF}$ in fluoroaromatics is between 5 and 6 D./Å.¹⁵

The spectra as shown above are consistent with D_{3d} molecular symmetry. However, small deviations from this symmetry toward, for example, C_{2v} symmetry would be expected to have little effect on the observed spectra. The vibrational perturbations are likely to be small at the best, and the intensity changes resulting from a relaxation of the selection rules insufficient to avoid confusion with changes resulting from molecular interactions. For example, there is little change in the spectra of biphenyl in going from the solid phase (D_{2h} symmetry) to the solution phase (inter-ring angle $\sim 30^\circ$) even though steric interactions and π conjugation undoubtedly are decreased.¹⁶

In summary, three factors indicate that Mg-

(15) D. Steele and D. H. Whiffen, *Trans. Faraday Soc.*, **56**, 177 (1960).

(16) D. Steele and E. R. Lippincott, in press.

(C_5H_5)₂ should be considered as an essentially covalent compound, rather than ionic, with d^2sp^3 hybridization to the Mg atom. The great similarity of the spectra of $Mg(C_5H_5)_2$ in both solid and solution phases to that for ferrocene is in itself an argument for the covalent bonding in the magnesium compound. There are no features in the solution spectrum which would suggest that there has been a change in bonding from that of the solid form. Thus the same molecular units must be present in the solid phase as have been observed in solution.

The measured intensity of the antisymmetric ring-metal stretching in $Mg(C_5H_5)_2$ is definitely inconsistent with the assumption of an ionic structure (C_5H_5)⁻ Mg ⁺⁺(C_5H_5)⁻ or appreciable contribution from this structure.

The great solubility of the magnesium compound in benzene (about one g. in 5 ml. of benzene) and cyclohexane is another factor which may be taken as an additional evidence supporting the covalent nature of the molecule.

It may be concluded that the bis-cyclopentadienylmagnesium resembles the corresponding iron compound (ferrocene) in structure and in bonding. However, the much weaker ring-to-metal bond observed in the $Mg(C_5H_5)_2$ may be considered responsible for the so-called "ionic" behavior of the compound, despite the fact that the bonding is essentially covalent in nature.

Acknowledgments.—The financial assistance from the Atomic Energy Commission and the National Science Foundation is gratefully acknowledged.