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VIBRATIONAL SPECTRA AND STRUCTURE OF BIS(CYCLOPENTADIENYL)MAGNESIUM

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Summary

Raman and infrared spectra have been obtained for $(C_5H_5)_2Mg$. The Raman results are for the solid and melt forms and include depolarization measurements. Infrared data for the solid at 25 K cover the range 400—3200 cm^{-1}. The analysis of the data obtained leads to the conclusion that the M—Cp bond in $(C_5H_5)_2Mg$ is mainly ionic in nature. The assignment of some fundamentals is revised.

The nature of bonding in bis(cyclopentadienyl)magnesium (magnesocene) still attracts considerable attention. While being a typical sandwich compound [1,2], magnesocene differs significantly from classical dicyclopentadienyl complexes of transition metals, such as ferrocene and other complexes with predominantly covalent bonding. The conductivity of solutions in liquid ammonia, the ease of ligand exchange with $FeCl_2$ leading to formation of ferrocene, certain features of the photoelectron spectra and other properties of magnesocene lead to the conclusion that the M—Cp bond (Cp = cyclopentadienyl) is primarily of ionic nature [3—5]. Several authors [2,6] on the other hand, argue the covalent nature of the M—Cp bond on the basis of the volatility of the complex, its high solubility in organic solvents, the relatively low intensity of the ν(M—Cp) band in the IR spectrum and data from quantum-chemical calculations of charge distribution.

To obtain new data on the nature of the M—Cp bond we investigated the vibrational spectra of solid and molten magnesocene. IR absorption spectra have been reported [3,6,7] and the Raman spectrum of magnesocene solution has been studied [6]. However, no polarisation data, required for interpretation of Raman spectra, have been found in the literature and the IR absorption spectra reported contain strong bands that obviously belong to decomposition products. Therefore we thought it necessary to repeat the IR spectra measurements in conditions excluding complex decomposition.

Magnesocene was prepared by interaction of metallic magnesium with cyclopentadiene according to [8]. The substance was purified by repeated vacuum sublimation. Large colourless crystals of the complex were obtained after slow sublimation without any noticeable traces of decomposition.

IR absorption spectra were recorded on a Hitachi Perkin—Elmer 225 spectrophotometer, with spectral width of the slit not exceeding 1.0—1.5 cm^{-1}, in the 400—1500 cm^{-1} region. Samples were prepared by vacuum deposition (10^{-5} mmHg) on KBr windows placed in a Displex low-temperature apparatus. Raman spectra were measured on Coderg PHO and T-800 spectrometers equipped with He Ne and Ar^+ lasers, respectively. Samples were studied in vacuum-sealed thin capillaries. The recording of melt spectra and low-temperature measurements were performed using devices provided in the equipment of the instruments. The results of measurements are presented in Table 1.

The Raman spectra of crystalline magnesocene display more lines than the solution spectrum described in [6]. The spectra include quite strong 1063 and 1342 cm^{-1} lines typical of Cp-complexes. The 1163 cm^{-1} line reported in [6] as being strong and assigned to in-plane bending $\beta(CH)(E_{2g})$ vibrations * is not observed. The IR absorption spectra are also more complex, although several bands that are attributed to magnesocene in [6,7] but actually belonging to cyclopentadiene, are absent. In the recorded spectrum only traces of the most strong cyclopentadiene band at 664 cm^{-1} are observed [9].

The Cp-ligand bands in magnesocene are observed at approximately the same frequencies as in the vibrational spectra of other Cp-complexes with the exception of the out-of-plane $\rho(CH)$ bending mode that is displayed at frequencies characteristic of complexes with ionic bonding [10]. Also the frequency of the $\nu(CC)$ (E_{1u}) vibration is somewhat higher than in covalent MCp_2 complexes (1425 instead of 1400—1410 cm^{-1}).

Certain interesting features are observed in the intensity distributions of Raman and IR absorption spectra. The line at 1014 cm^{-1} ($\beta(CH)$) is very weak and the line in the 1400 cm^{-1} region ($\nu(CC)$) is absent, whereas in the Raman spectra of ferrocene, ruthenocene and osmocene they are both quite strong [11]. This peculiarity, which is also observed in the spectra of manganocene [12] and of tricyclopentadienyl complexes of the rare earth metals [13], is very significant since both vibrations are forbidden for the free $C_5H_5^-$ ion (vibrations of E'_1 symmetry types of the D_{5h} group). Their appearance in the Raman spectra may be due to perturbation of the Cp-ligand by the metal atom in the CpM moiety. Since these lines are weak, the perturbation affect of the metal is slight and the Cp-ligand spectrum retains features of the $C_5H_5^-$ spectrum.

Bands at 760—800 ($\rho(CH)$) and at 1000 cm^{-1} ($\beta(CH)$) are very strong in the IR spectra, while the bands at 1100 cm^{-1} ($\nu(CC)$) are very weak. Since the first two group of bands correspond to vibrations allowed in the IR spectrum of $C_5H_5^-$ (E'_1) and 1100 cm^{-1} bands are forbidden (A'_1), evidently the IR spectrum of magnesocene also has features similar to the $C_5H_5^-$ spectrum. It should be noted that these features have been reported for IR spectra of ionic Cp-complexes [2,14].

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* Magnesocene vibrations are classified according to the D_{5d} symmetry group throughout this paper.

TABLE 1

VIBRATIONAL SPECTRA OF MAGNESOCENE

Raman					IR [a] crystal (low temp.)		Assignment
Melt [b]			Crystal [c] (room temp.)		ν	I	
$\Delta\nu$	I	ρ	$\Delta\nu$	I			
			69	w			
			85	vw			
			118	vw			
			156	w	[d]		
189	72	dp	207	s			ν_{16} (E_{1g})
			218	s			
218	20	p	233	m			ν_4 (E_{1g})
					461	s	ν_{11} (A_{2u})
					524	m	ν_{21} (E_{1u})
					614	vw	χ(CCC)
					663(sh)	vw	admixture of cyclopentadiene
750	6	dp	758	m	759	vs	ρ(CH)
			768	m	768	vs	
778	1	dp?	783	w	788	vs	
					798	s	
832	4	p			824	w	
			853?	w	850	w	
					853	w	
					871	m	γ(CCC)
					887	w	cyclopentadiene ?
					967	vw	
					1004	s	β(CH) (E_{1g}, E_{1u})
1014	1	dp			1007	s	
1063	5	dp	1061	m	1060	w	β(CH) (E_{2g}, E_{2u})
			1103	w	1098	w	ν(CC) (A_{1g}, A_{2u})
1113	100	p	1110	vw	1105	w	
			1125	w	1118	w	
					1256	m	β(CH) (A_{1u}) ?
1264	1	p					
					1290	vvw	
			1327	w			ν(CC) (E_{2g}, E_{2u})
1342	6	dp	1342	s	1337	vw	
					1425	vw	ν(CC) (E_{1g}, E_{1u})
					1448	vvw	
3077	2	dp	3076	m	3064	w	ν(CH)
			3091	w	3084	vw	
3105	7	p	3102	s			

[a] Spectrum of overtones in the 1450—3000 region is omitted. [b] The intensities are relative and photometrical; no correction was carried out for the spectral sensitivity of the spectrometer. [c] The region up to 250 cm^{-1} was measured at the temperature of liquid nitrogen. [d] The region up to 400 cm^{-1} was not measured.

Thus, examination of the vibrational spectrum of the ligand leads to the conclusion that the M—Cp bond in magnesocene is mainly ionic in nature.

Assignment of the Cp-ligand spectrum presented in Table 1 differs in two aspects from the generally accepted interpretation.

(1) Transitions in the 1060 cm^{-1} region are assigned to β(CH) vibrations, where-

as they are usually assigned after Lippincott and Nelson [15] to ρ(CH) vibrations. We have discussed this question in a previous work while studying the spectra of Cp-ligand vibrations in various Cp-complexes [16].
(2) The weak line at 1264 cm^{-1} is polarised like the corresponding lines in other Cp-complexes [12,17]. Therefore we assigned it, as in previous cases, to the overtone of one of the out-of-plane ring vibrations (E_{2g}?) strengthened by Fermi resonance with ν(CC) (A_{1g}) vibration.

Interesting features are also observed in the region of skeletal vibrations. In contrast to [6], we assigned the symmetrical ν(M—Cp) (A_{1g}, ν_4) vibration to the relatively weak but polarised line at 218 cm^{-1} and not to the strong but depolarised 189 cm^{-1} line. Thus in magnesocene, as in the case of nickelocene [14], the values of ν_4 (A_{1g}) and ν_{16} (E_{1g}) vibration frequencies are reversed. Moreover, in magnesocene the intensities of symmetrical and nonsymmetrical vibrations are also reversed, i.e. $I(\nu_4) < I(\nu_{16})$. This is a rather unusual phenomenon in Raman spectroscopy.

Frequency inversion can be considered as additional confirmation of the ionic nature of the M—Cp bond in magnesocene. Provided that electrostatic interaction contributes considerably to the M—Cp bonding, the force constant of tilting vibrations (E_{1g}) should be smaller than the force constant of symmetric stretching vibrations (A_{1g}) all other conditions being equal.

In the low-frequency region of the magnesocene IR spectrum two bands are observed that are apparently due to ν_{11} (A_{2u}) and ν_{21} (E_{1u}) skeletal vibrations, antiphase analogues of Raman active ν_4 and ν_{16} vibrations. In [6] the ν_{11} vibration was assigned to the 461 cm^{-1} band and ν_{21} vibration to the 524 cm^{-1} band. However, without additional data the reverse assignment can not be discarded. Both bands are rather weak and, on the basis of the low integrated intensity of the 461 cm^{-1} band as compared with the value calculated from the zero approximation of the effective charge model, it was concluded in [6] that the Mg—Cp bond is covalent in nature. But the zero approximation of the effective charge model may give erroneous results when applied to stretching modes.

Let us consider the expression for the increment of the dipole moment of the vibrating molecule in the effective charge model.

$$\Delta\mu = \Delta\left(\sum_{\alpha}\vec{R}_{\alpha}E_{\alpha}\right) = \sum E_{0\alpha}\Delta\vec{R}_{\alpha} + \sum_{\alpha}\vec{R}_{0\alpha}\sum_{\beta}\left(\frac{\partial E_{\alpha}}{\partial\vec{R}_{\beta}}\right)\Delta\vec{R}_{\beta} \tag{1}$$

The first term in the right-hand side of eq. 1 corresponds to the zero approximation. The second term accounts for the change of effective charge due to displacement of atoms from equilibrium positions. For stretching vibrations the second term is not so small in relation to the first term and sometimes exceeds it many-fold, for example, in the case of the CO stretching vibrations in carbonyl complexes of metals [18].

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