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THE RAMAN SPECTRUM AND STRUCTURE OF DICYCLOPENTADIENYLBERYLLIUM

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Summary

The Raman spectra of solid and liquid dicyclopentadienylberyllium are described. They suggest the presence of two π-bonded rings in the molecule, one *pentahapto* and one *polyhapto* coordinated to the Be atom.

Introduction

In 1951 the first metallocene, Cp_2Fe, was discovered [1], and shown to have the sandwich structure of D_{5d} symmetry (Fig. 1A). Dicyclopentadienylberyllium, Cp_2Be, the smallest metallocene, was first synthesized by Fischer and Hoffmann in 1959 [2]. In 1964 Haaland et al. [3,4] concluded from electron diffraction studies that in the gas phase Cp_2Be had a structure of C_{5v} symmetry (Fig. 1B), highly unusual for metallocenes. On the other hand, Wong et al. [5, 6] showed by X-ray diffraction studies that in the solid state Cp_2Be had a slip sandwich structure. Wong et al. [5] proposed a σ—π bond system in the molecule at low temperatures (Fig. 1C). However, Drew and Haaland [7] interpreted Wong's results differently, suggesting the presence of two π-bonded rings in the molecule, one *pentahapto* and one *polyhapto* coordinated to the Be atom (Fig. 1D).

The structure of Cp_2Be was also investigated by means of vibrational spectroscopy. Fritz et al. [8,9,10] concluded from the IR spectrum of Cp_2Be in the solid state that the molecule contained two equivalent centrally σ-bonded rings. After the structure of C_{5v} symmetry has been proposed for the gas phase [3,4], Fritz and Sellmann [11] and McVicker and Morgan [12] suggested the same structure for the solid state and solutions on the basis of new IR data. McVicker and Morgan found the model $(CpBe)^+ Cp^-$ to be the most consistent with their IR data for solid Cp_2Be.

The IR spectra mentioned above are not consistent. Furthermore, no papers

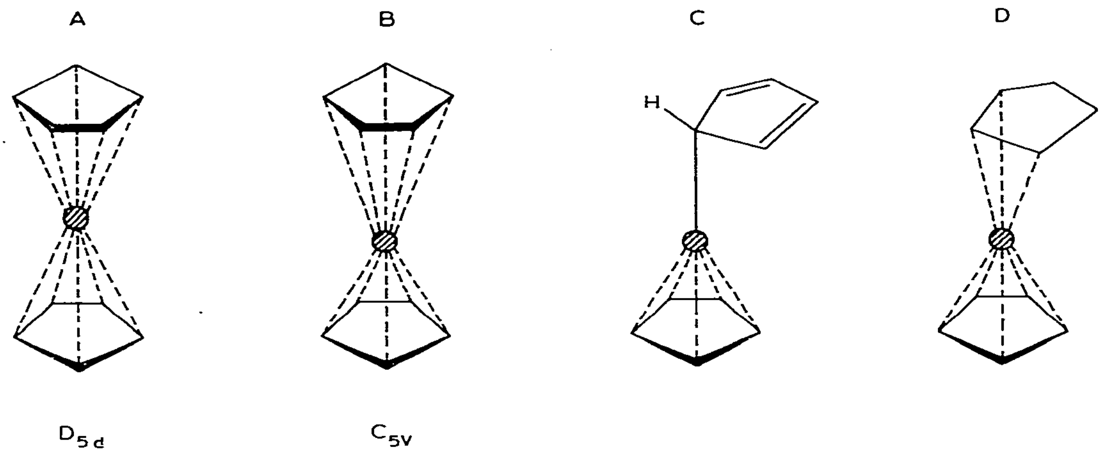

Fig. 1. Possible structures of Cp_2Be.

concerned with the vibrational spectra of Cp_2Be have appeared since the slip sandwich structure was established by X-ray diffraction [5,6]. Thus, there is a disagreement between X-ray and IR results. Moreover, the Raman spectrum of this compound has not been reported. We thus decided to undertake measurements of Raman spectra of Cp_2Be in order to remove the inconsistency between vibrational and X-ray data and provide a new approach to the question of the bonding in this compound.

Results and discussion

The Raman spectra of solid Cp_2Be at —160° C and 25° C and the spectrum of liquid Cp_2Be at 65° C were recorded. They are shown in Fig. 2. The band positions are listed in Table 1.

We have considered the four models presented in Fig. 1 in analysing the obtained spectra. The simplest spectrum is expected for the structure of the highest symmetry, A. The spectrum obtained is much more complicated than the spectra of compounds of D_{5d} symmetry, e.g. ferrocene [14] or magnesocene [15]. Thus we conclude that the molecule contains two nonequivalent Cp rings.

The obtained spectrum contains all the bands corresponding to the normal modes of one Cp ring of local C_{5v} symmetry π-bonded to Be atom, see Table 1. Their positions and intensities are very similar to those observed in the spectra of monocyclopentadienylberyllium derivatives which are believed to have a CpBe moiety of C_{5v} symmetry as CpBeCl [16,17,18], CpBeBr, $CpBeCH_3$, CpBeC≡CH [18].

The character of the second Cp ring is not so clear. For the model B we expect two sets of bands corresponding to two different Cp rings, both of local C_{5v} symmetry, as assumed in the analyses of the IR spectrum of Cp_2Be [11, 12]. However, in our opinion the existence of a polarized band at 3000 cm^{-1} in the C—H stretching region and polarized bands in the region 1380—1420 cm^{-1}, which are unexpected for a Cp ligand of C_{5v} symmetry, excludes this model.

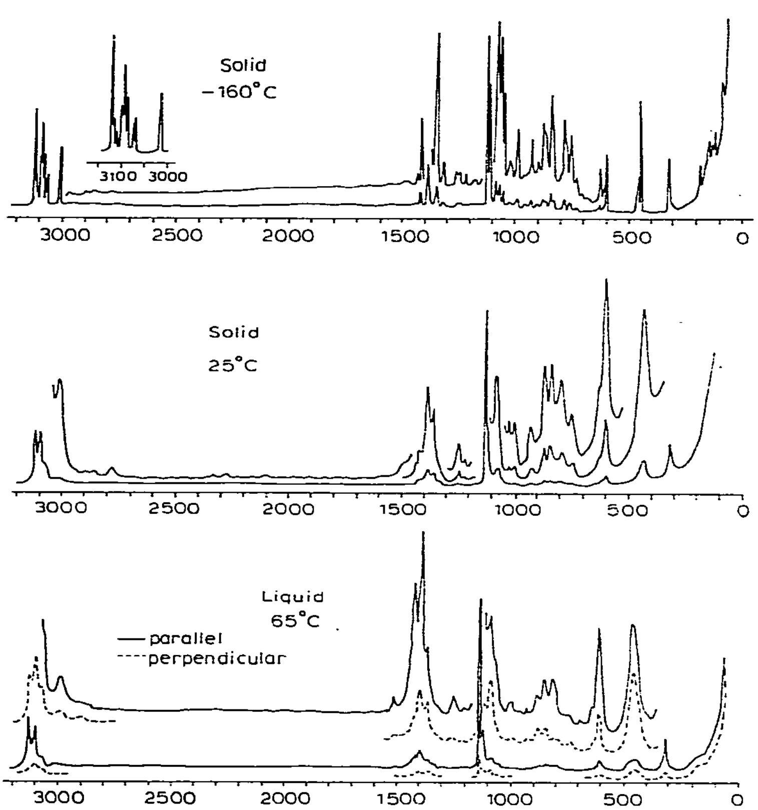

Fig. 2. Raman spectra of Cp_2Be.

The model with an electrostatically bonded second ring of local D_{5h} symmetry is rejected for similar reasons.

In the case of the σ-bonded ring, model C, a more complicated spectrum is expected [10,19,20]. The most characteristic bands should appear in the C—H stretching region 2800—3000 cm^{-1} (unexpected for any other models), and in the C=C stretching region, 1500—1600 cm^{-1}. We have not observed such bands in our spectra and the model C has accordingly been rejected.

Thus we are left with model D, with *pentahapto/polyhapto* bonded Cp rings, which we assume to be most consistent with our data. The only published vibrational spectra of a *polyhapto*-bonded Cp ring of which we are aware are those presented by Stadelhofer et al. [21] for $CpAlEt_2$ and $CpGaEt_2$. These are similar to those obtained for Cp_2Be, especially in the C—H stretching region.

Our conclusions can be summarized as follows: (a) there are two different Cp rings in the molecule of solid and liquid Cp_2Be, (b) one of the rings possesses C_{5v} local symmetry, (c) the second ring deviates from the local C_{5v} symmetry and is probably *polyhapto*-bonded to the metal, and (d) the proposed bond system of Cp_2Be is consistent with X-ray data obtained by Wong et al. at room temperature [6]. We have not observed any significant differences between the spectrum of Cp_2Be in the solid at —160 and 25°C and that of the liquid at 65°C. Hence in the case of the crystals at low temperature we are inclined to

TABLE 1. RAMAN SPECTRAL FREQUENCIES (cm^{-1}) OF Cp_2Be

Solid −160°C	Solid 25°C	Liquid 65°C	Polarization ratio	Proposed assignments for CpM (C_{5v}),[13]		
				Normal mode	Symmetry	Approximate description
87 s						
124 s						
136 s						
150 s						
165 m						
187 s						
320 s	313 s	313 s	0.23			ν(Cp—Be) [a]
447 vs	430 s(br)	447 m	0.76	$\nu(10)$	E_1	ν(Cp—Be)
461 s						
600 s	598 m	598 m	0.37			ν(Cp—Be) [a]
630 vw	627 w(sh)	628 vw(sh)	0.60	$\nu(16)$	E_2	χ(CCC)
736 vvw						
762 w	750 vw	745 vvw	0.80			
780 w(sh)						
	795 w	795 w	0.27	$\nu(3)$	A_1	ρ(CH)
789 w						
838 w(sh)						
	841 w	839 w	0.50	$\nu(15)$	E_2	ρ(CH)
846 w						
869 w(sh)						
	870 w	873 w	0.75	$\nu(9)$	E_1	ρ(CH)
883 w						
905 vvw						
934 vw	930 vw	925 vvw	0.75	$\nu(14)$	E_2	λ(CCC)
996 w	1001 vw	994 vw	0.50			
1030 vw	1026 vw	1030 vw(sh)		$\nu(8)$	E_1	β(CH)
1058 m		1055 w(sh)	0.30			
1075 m						
	1083 m	1082 m	0.68	$\nu(13)$	E_2	β(CH)
1089 m						
1118 vs	1118 s(sh)	1116 s(sh)	0.15			
1129 vs	1127 vs	1130 vs	0.12	$\nu(2)$	A_1	ν(CC)
1227 vvw	1225 vvw					
1256 vvw						
	1249 vw	1246 vw	0.28	$2\nu(16)$	A_1	
1267 vvw						
1325 vw						
1356 m	1360 m	1362 m	0.75	$\nu(12)$	E_2	ν(CC)
1390 s	1388 m	1395 m	0.28			
1420 w	1420 w	1420 m	0.19			
1440 vvw	1440 vw(sh)			$\nu(7)$	E_1	ν(CC)
	1506 vvw		0.10	C_5H_6 imp.		
	2783 vvw					
	2869 vvw					
3013 s	3020 w	3002 w(br)	0.25			
3069 m						
	3070 m(sh)	3074 m(sh)	0.60			
3076 m						
3087 s						
3094 s	3102 s	3100 s	0.25			
3100 m(sh)						
3110 m				$\nu(6)$, $\nu(11)$	E_1, E_2	ν(CH)
3116 m(sh)						
3122 s	3123 s	3128 s	0.15	$\nu(1)$	A_1	ν(CH)

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[a] We believe, those two bands belong to symmetric stretching $\nu(h^5$-Cp—Be) and $\nu(h^2/h^3$-Cp—Be), but we failed to assign them specifically. We found [18] the bands corresponding to $\nu(h^5$-Cp—Be) in the spectra of CpBeX as follows: CpBeCl 313 cm^{-1}, CpBeBr 246 cm^{-1}, $CpBeCH_3$ 396 cm^{-1}, CpBeC≡CH 351 cm^{-1}.

accept the *pentahapto/polyhapto* bond description proposed by Drew and Haaland, rather than the σ—π bond description proposed by Wong et al. [5].

Experimental

Cp_2Be was obtained by the method described by Fischer et al. [2] and purified by vacuum transfer. The melting point of Cp_2Be was 59—60° C, its purity was also checked by mass spectrometry.

The Raman spectra were recorded on a Coderg Spectrophotometer, with the 4880 Å line of an Ar ion laser as exciting radiation.

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