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Vibrational spectra and structure of dicyclopentadienylzinc

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Abstract

The infrared (4000–50 cm^{-1}) and Raman spectra of dicyclopentadienylzinc (Cp_2Zn) in the solid state and in a tetrahydrofuran (THF) solution have been studied and discussed in connection with the structure of Cp_2Zn. The slip-sandwich $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Zn$ molecular structure in solution is proposed based on of the analysis of the spectra in the regions of metal–ligand and out-of-plane ρ(CH) bending vibrations. The assignment of vibrational frequencies is proposed. The comparison of the Raman spectra at 300 and 20 K shows that Cp_2Zn crystals undergo a phase transition upon lowering the temperature. © 1998 Elsevier Science S.A.

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1. Introduction

Vibrational spectra of metal biscyclopentadienyl complexes $(C_5H_5)_2M$ (Cp_2M) have been investigated in detail and discussed in a number of reviews and monographs [1–5]. It has been shown that the spectrum of the coordinated Cp ligand depends on the type of the metal–ligand coordination (pentahapto η^5 or monohapto η^1) and on the nature of the metal–ligand bond (ionic, central π- or σ-bond). However, the spectral characteristics of some Cp complexes, dicyclopentadienylzinc among them, are markedly different from those of typical sandwich complexes.

Cp_2Zn was firstly synthesised by Fischer and coauthors [6] and characterised by seven bands in the IR spectrum, which gave reason to suggest the ferrocene-type sandwich structure. In Fritz's review [5] Cp_2Zn was classified as a typical cyclopentadienyl π-complex with C_{5v} symmetry of the Cp ligand. Lorberth [7] proposed structures with a central σ-bond for Cp_2M complexes (M = Zn, Cd, Hg) on the basis of ^1H NMR data. However, Burlitch [8] used the formula $(\eta^1\text{-Cp})_2Zn$ by analogy with Cp_2Hg. So, the incomplete IR-spectral data (only for solid samples in the 4000–400 cm^{-1} region) have led to contradictive opinions.

The crystal structure of Cp_2Zn was determined in 1985 by X-ray diffraction [9], which closed the discussion about the Cp_2Zn structure in the solid state. It was found that a Cp_2Zn crystal consists of infinite bent chains of zinc atoms with bridging Cp ligands. Every zinc atom is connected with two bridged Cp groups and carries the terminal Cp group. Taking for granted that the interatomic distances less than 2.5 Å (from 2.04 to 2.41 Å) correspond to the chemical bonds Zn–C, each of the rings is bound to the metal atom by two carbon atoms (η^2-coordination).

It is interesting to compare the vibrational spectra of such Cp ligands with those of mono- and pentahapto-coordinated rings. The structure of the isolated Cp_2Zn molecule is unknown. It may differ essentially from the structure in crystal. Thus for the relative molecule $CpZnCH_3$ the structure $(\eta^5\text{-}C_5H_5)ZnCH_3$ with C_{5v} symmetry was determined by electronography in the gas phase [10]. But that molecule forms polymeric chains with the bridging Cp rings in the crystal [11]. Detailed vibrational spectral data for Cp_2Zn are not available.

In the present work we studied the IR spectra of solid Cp_2Zn in mid- and far-infrared regions (4000–50 cm^{-1}) at room temperature and the Raman spectra at 300, 77 and 20 K. In order to obtain information on the molecular structure of monomeric Cp_2Zn we investigated the IR and Raman spectra of Cp_2Zn solutions in tetrahydrofuran (THF).

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2. Experimental

Dicyclopentadienylzinc was synthesised and purified by the method developed earlier for tricyclopentadienyllantanides [12]. A mixture of CpNa and $ZnCl_2$ with a molar ratio of 2.5 : 1 was stirred in THF solution during 7–8 h at 65–70°C. At the final stage of the synthesis Cp_2Zn was separated by sublimation in vacuo at 150–160°C. The thermal destruction of Cp_2Zn takes place at higher temperatures. Dicyclopentadienylzinc was obtained as white crystals ($>$ 70% yield), m.p. 190 ± 2°C with small decomposition.

The sample preparation and spectral measurements were performed under the conditions precluding any contact with oxygen and moisture [13]. IR spectra were recorded on Bruker IF 5-113v and IFS-45 FT-IR spectrometers at room temperature in Nujol and Fluorolube mulls and in THF solutions.

The Raman spectra of the crystalline samples at 300, 77 and 20 K in vacuum-sealed glass thin-walled ampoules of about 3 mm in diameter were measured with a Ramanor-HG-2S spectrometer using excitation with 5145 A line of Ar^+-laser.

3. Results and discussion

The spectra measured, the frequencies and relative intensities of the bands in the vibrational spectra of Cp_2Zn and their assignments are presented in Fig. 1 and Table 1. It is known [1–5] that inner vibrations of the Cp ligands in cyclopentadienyl complexes are arranged in the region above 600 cm^{-1}, and metal–ligand vibrations (skeletal vibrations) below 500 cm^{-1}. So it is possible to discuss the ligand and skeletal modes separately.

4. Spectra of solid Cp_2Zn

4.1. Cyclopentadienyl ligand vibrations

It is known that the vibrations of the η^5-Cp ligand with the local symmetry C_{5v} are quite characteristic. They and arranged in the regions: 3100 cm^{-1} (ηCH of symmetry classes A_1, E_1 and E_2), 1400–1450 cm^{-1} (νCC, E_1), 1350 cm^{-1} (νCC, E_2), 1100 cm^{-1} (νCC, A_1), 1050 cm^{-1} (δCH, E_2), 1000 cm^{-1} (δCH, E_1), 900 cm^{-1} (γCCC, E_2), 700–850 cm^{-1} (ρCH, A_1, E_1, E_2), 600–620 cm^{-1} (χCCC, E_2). The frequencies of in-plane vibrations are relatively little sensitive to the nature of the metal–ligand bond, however, their intensities can vary significantly. So the frequencies of the ring breathing modes (νCC, A_1) are rather strong in the IR spectra of complexes with the central π-bond, but they are very weak or not observed in the case of ionic compounds. In the Raman spectra this vibration always gives rise to a very strong line. The bands of the γCCC, χCCC, νCC(E_2) modes are very weak in both IR and Raman spectra. The bands corresponding to ρCH out-of-plane vibrations are very strong in the IR spectra, and their frequencies are the most sensitive to the metal–ring bond nature. With an increase in the metal–ligand bond polarity, the ρCH frequencies decrease (from 820 cm^{-1} for Cp_2Fe to about 750 cm^{-1} for compounds with the ‘‘central σ-bond’’). The minimal

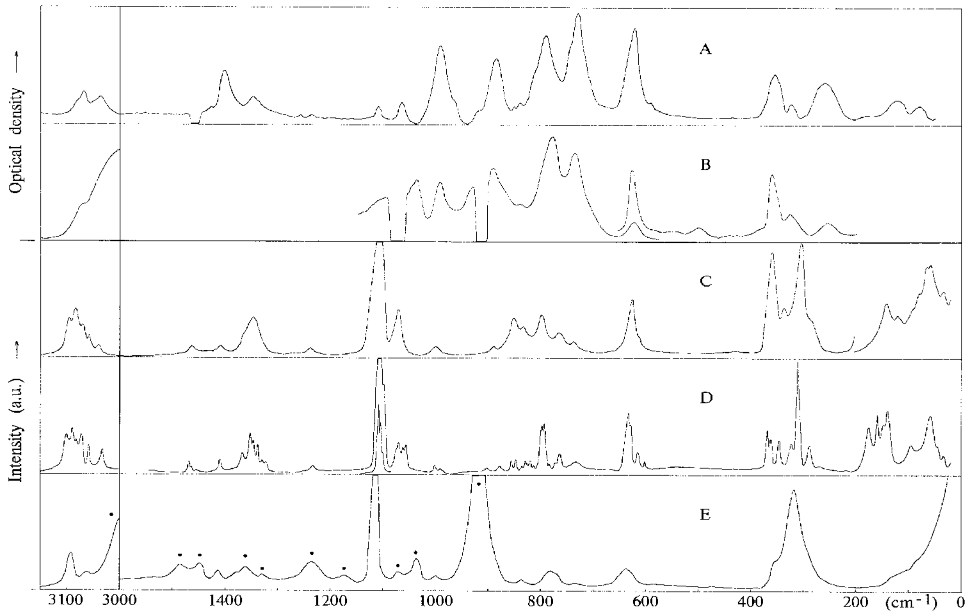


Fig. 1. Vibrational spectra of dicyclopentadienylzinc: IR spectra in nujol mull (A) and in THF solution (B); Raman spectra of polycrystals at 300 K (C), 20 K (D), and of THF solution (E). ●, THF bands.

value of 686 cm^{-1} was observed in the spectrum of the cyclopentadienyl anion [13–15].

The monohapto-Cp ligand may be considered as a substituted cyclopentadien. The characteristic spectral features of the η^1-Cp ligand are the bands of symmetric and asymmetric vibrations of the C=C double bonds (ν^{sym}C=C and ν^{asym}C=C) in the region 1500–1600 cm^{-1} and the νCH band of the sp^3-hybridised carbon atom at about 2950 cm^{-1}. Furthermore in contrast to η^5-complexes, the intensive bands of the ρCH vibrations in the IR spectra are in the region 600–750 cm^{-1}. The bending modes of the Cp ring appear as strong IR bands at 850–950 cm^{-1}, and the δCH modes manifest themselves as intensive bands in the region 1200–1370 cm^{-1}. Both cyclopentadien and η^1- and η^5-Cp ligand ring breathing modes have a frequency of about 1100 cm^{-1}. The νC=C bands in the spectra of some η^1-complexes are weak and sometimes not observed in both IR and Raman spectra [16].

The terminal η^1- and η^5-coordinations are not the only plausible types of metal–ring bonding. Sometimes Cp complexes contain η^5/η^5-Cp ligands bridging two metal atoms as in ‘‘triple-decker’’ sandwich complexes of the $\mathrm{Cp_3Ni_2^+PF_6^-}$-type [17]. The same type of bridged ligands occurs also in crystals of some Cp complexes, for example, complexes of In and Tl [18,19]. The vibrational spectra of such ligands are typical of η^5-complexes. Indeed, in the spectra of $\mathrm{Cp_3Ni_2^+F_6^-}$ the frequencies of the bridged ring are arranged in the same regions as those of the terminal Cp groups, whilst some of them are 10–25 cm^{-1} shifted.

Another group of compounds is represented by complexes with the ‘‘slip-sandwich’’ structure containing the ‘‘peripheral’’ metal–carbon bond. Such a type of structure was first observed in crystals of some Cp complexes. Then it was shown that the slip-sandwich structure occurs not only in the crystal state. An example of this type of bonding is $\mathrm{Cp_2Be}$, for which the slip-sandwich structure was presumed from the IR spectra not only in the solid state but in the gas phase as well [20,21]. Such a bond differs from the common metal–carbon σ-bonds by the value of the valent angle at the carbon atom connected with metal, which differs significantly from the tetrahedral angle. In a number of cases the angle between the M–C bond and the ring plane is close to 90°. Upon this coordination the C=C bonds of the Cp ring are still delocalised and the νC=C bands of cyclopentadiene are not observed in the vibrational spectra. The hybridisation of the carbon atom, connected with the metal, is sp^2 rather than sp^3 and νCH bands in the region below 3000 cm^{-1} are absent in the spectra. Along with the terminal peripheral Cp–M bonds, the bridged peripheral η^1/η^1-bonds also occur in crystals (see Ref. [21] and references therein).

The frequencies of the in-plane $\mathrm{C_5H_5}$ ligand vibrations are similar for different types of coordination, however, their intensities can vary essentially due to changes in symmetry. So, the bands of the ring bending vibrations near 900 cm^{-1} for η^5-complexes are very weak in both IR and Raman spectra, but they provide strong IR absorption for other types of coordination. Frequencies and intensities of the out-of-plane CH and ring modes are much more sensitive to changes in the M–Cp bonding. Different types of coordination of the Cp rings to metal are shown in Fig. 2. It should be remembered that the structures shown represent the extreme cases. Actually any intermediate states are probable to exist.

Before considering the spectra of $\mathrm{Cp_2Zn}$ let us consider again its crystal structure. The authors of Ref. [9] concluded that terminal and bridged Cp ligands of the η^2-type are present in the solid state. They postulated that a Zn–C distance shorter than 2.5 Å may be a criterion for the chemical bond. However, a careful inspection of the structure shows that Zn–C bond lengths vary within rather wide limits. Terminal Cp groups form two bonds with lengths of 2.04–2.08 and 2.33–2.48 Å. The difference in the bond lengths is so significant that the second distance may be considered as a ‘‘short unbonding contact’’ suggesting that the terminal ligands look like η^1-coordinated in the vibrational spectra. There are several types of bridged ligands in the crystal state due to two crystallographically independent types of the metal atoms Zn(1) and Zn(2). Some of these ligands are placed between the Zn atoms of the different types and are bound to the Zn(1) and Zn(2) atoms by bonds with lengths of 2.04 A and 2.19 Å, respectively. The other Zn–C distances are significantly longer which permits to suppose that these ligands form the peripheral η^1/η^1-bridged bonds. Bridging ligands, located between the zinc atoms of the same type, are disordered in the crystal, but they also have a η^1/η^1-bridged structure. Thus, it appears that the $\mathrm{Cp_2Zn}$ crystal contains η^1-terminal and η^1/η^1-bridging ligands.

Let us consider the spectra of solid $\mathrm{Cp_2Zn}$ at room temperature. These have some interesting peculiarities. Firstly, the spectrum is much more complicated than it might be expected for the central type of coordination. This fact permits to rule out the $(\eta^5\text{-Cp})_2\mathrm{Zn}$ structure. Nevertheless, the IR spectrum contains absorption bands in the regions typical of η^5-Cp rings: 3096 and 3085 cm^{-1} (ηCH), 1106 cm^{-1}, (ν_{ring}), 1009, 986 cm^{-1} (βCH), 780, 728 cm^{-1} (ρCH). Corresponding bands are present in the Raman spectrum too. The relationship between the intensities in the IR and Raman spectra is similar to that for η^5-Cp compounds: the band of the breathing ring vibration at 1107 cm^{-1} is weak in the IR spectrum and strong in the Raman spectrum, the bands of out-of-plane CH modes in the region 700–800 cm^{-1} are strong in the IR spectrum and weak in the Raman spectrum. The bands at 1354, 1061, 914 and 603 cm^{-1} corresponding to the $\mathrm{E_2}$ class forbidden in the IR

Table 1
Frequencies (cm^{-1}) in vibrational spectra of dicyclopentadienylzinc

Crystal			THF solution, 300 K		Assignment
Raman, 20 K	Raman, 300 K	IR, 300 K	Raman	IR	
3099m	3098w	3096sh	3090m,p (0,10)		
3088m	3086m	3085sh			
3080w		3079sh		3076w	
3072m	3072sh			THF	νCH
3057w	3058vw	3067m	3063w,dp (0,61)		
3030w	3038w	3046vw			
		3038w			
1475vw					
1472vw	1470vw				ν_{ring}
1460vw					
		1440sh			
1414w	1416w	1409m	1416vw	1416w	
1373w	1370sh		1380vw		
1357m					ν_{ring}
1352w	1352m	1352vw			
1343w		1341sh			
1333vw					
1327vw					
1238vw,br	1240vw,br	1258vw			
		1238vw			
1112vs			1112vs,p (0,06)	1099w	
1107vs	1107vs	1106w			ν_{ring}
1103sh					
1074sh					βCH
1069w	1068m	1061w		THF	
1062w					
1057w				1032m	
1000vw	998vw,br	1009sh	995vw	990s	βCH
988vw		986s			
		961sh		960w	
		914vw		THF	
898vw			833w,dp (?)		
877w,br	886vw	878s		864s	δ_{ring}
852w					
844w	848m	843vw			
833vw		833vw			
825w	828w				
815vw					
810vw		802sh			
794m	793m				ρCH
792m		780vs	774m,p (0,21)	774vs	
762w	762vw		755sh		
730o.w,br	732vw	737sh		736s	
		728vs	715vw,dp		
628m			632m,p (0,20)		βCH
624sh	624m		624m,p (0,20)	622m	
608w	610sh	616vs	616sh		
597vw		603sh			
				494w	
364m				378vw	
358m	358s	349m		349m	tilt ZnCp
343m	335sh		344w,p (0,25)		νZn–Cp
322w		324w			
310s	305s		315s,p (0,10)	315w	νZn–Cp
287sh	280sh				
		263m		260vw	
176m	–			171vw,br	δCpZnCp
159m	–				
147w	142s		140vw		τCpZnCp?
138m		127w	135vw		
–	119m	112sh	115vw		

Table 1 (continued)

Crystal			THF solution, 300 K		Assignment
Raman, 20 K	Raman, 300 K	IR, 300 K	Raman	IR	
95w	90sh				lattice vibrations
–	80sh	85w			
–	68vs				
60m	62vs	60w			
46sh	–				
35w	37m				

spectra for C_{5v} symmetry are also close to the vibrational frequencies of the η^5-Cp ligand. These bands are usually weak for η^5-Cp complexes in both IR and Raman spectra.

Secondly, there are a number of ''extra'' bands in the spectra i.e. more than can be expected for the η^5-Cp ring. Primarily there are the bands at 878, 616 cm^{-1}, which are strong in the IR spectrum and weak or medium in the Raman spectrum. Similar bands are usually observed in the spectra of substituted cyclopentadienes and η^1-Cp complexes [1,2], and assigned to the stretching–bending ring modes and to out-of-plane CH modes, respectively. Thus the strong bands at 907, 885, and 646 cm^{-1} are present in the IR spectrum of $(\eta^1\text{-}C_5H_5)_2Hg$ [22]. However, the bands of $\nu C{=}C$ and bands νCH below 3000 cm^{-1} expected for η^1-coordination are absent in the spectra of Cp_2Zn. It was noted, that these bands may have low intensities and are not always observed for η^1-Cp compounds. On the other hand, the absence of these bands is in agreement with the slip-sandwich type of coordination. The presence of no less than five νCH bands in the region 3000–3100 cm^{-1} is also in agreement with such a structure.

The data presented indicate that the existence of the bands in the spectra characteristic of η^5-Cp coordination cannot be used as an evidence for the pentahapto coordination of the Cp ligand, if the additional bands are present, especially the strong bands in the region 600–900 cm^{-1}. The spectra of solid samples do not permit to distinguish the bands belonging to the bridging and terminal ligands. That is why it is interesting to compare the spectrum of the crystal with that of a solution, where the bridging ligands should be absent.

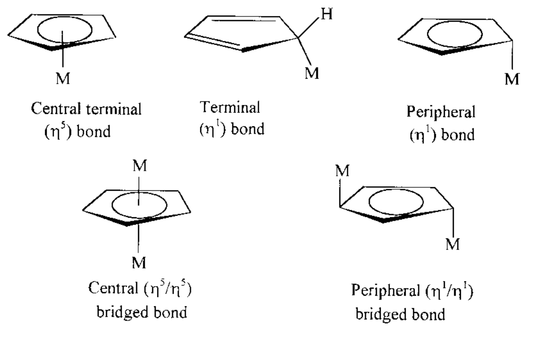


Fig. 2. The types of cyclopentadienyl ligand coordination with metal.

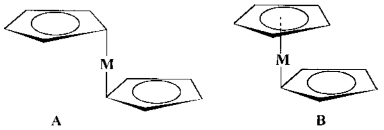
The IR and Raman spectra were measured in THF solutions, because $ZnCp_2$ is poorly soluble or insoluble in other solvents, which are more convenient from the spectroscopic viewpoint (CS_2, CCl_4 and etc.). Thus the IR spectral data for $ZnCp_2$ were not obtained in the regions, where the solvent has the strongest bands (2800–3000, 1050 cm^{-1}). In the other spectral regions, the solvent absorption bands were eliminated by computer subtraction.

The comparison of the spectra leads to an unexpected result: the solution and crystal spectra are closely similar. In the IR spectrum of the solution, all of the strong absorption bands observed for the crystal, practically remained. The frequency differences are, as a rule, less than 10 cm^{-1}. The spectra are similar not only in the region of the Cp ligand vibrations (above 600 cm^{-1}), but also in the region of the metal–ligand vibrations (200–500 cm^{-1}). The Raman spectra are also similar. It is seen from Table 1 that the ring breathing mode in the Raman spectrum gives rise to a strong band at 1107 cm^{-1} in the solid state and 1112 cm^{-1} in solution, in-plane CH deformations appear in the IR spectrum of the crystal at 986 cm^{-1} and in solution at 990 cm^{-1}. The strong IR bands of out-of-plane ρCH modes at 780, 737, 616 cm^{-1} in the spectrum of the crystal correspond to the bands at 774, 736 and 622 cm^{-1} in the spectrum of the solution. However, a number of weak bands observed in the solid state are lacking in solution, but it may be partially connected with the poor solubility of $ZnCp_2$ and also with breaking of polymeric structures.

An important conclusion follows from the data presented that the bridging and terminal Cp ligands cannot be distinguished in vibrational spectra of Cp complexes. In the case of η^5/η^5-bridges, it has been previously reported, for example for triple-decker $Cp_3Ni_2^+PF_6^-$ complexes [17]. Another example is Cp_2Pb, which has the $(\eta^5\text{-}Cp)_2Pb$ angular structure, and in the crystal state forms polymeric chains containing η^5-terminal and η^1/η^5-bridging ligands [23]. Its IR spectrum is similar to that of ferrocene. The same result follows for η^1/η^1-bridges from our data on $ZnCp_2$.

The molecular structure of $ZnCp_2$ is unknown. Since the bands of the Cp ligand characteristic of both the η^5- and η^1-types of bonding with metal, were found in the spectra, two slip-sandwich structures may be proposed:

(η^1-C_5H_5)$_2$Zn with two peripheral metal–ring bonds (type A) and (η^1-C_5H_5)(η^5-C_5H_5)Zn with one central bond and one peripheral bond (type B). These structures are shown below:



In principle, both structures seem probable because the η^5- as well as the η^1-type of coordination are known for zinc–Cp complexes. Half-sandwich $CpZnCH_3$, similar to Cp_2Zn, forms polymeric chains in the crystal state [11], but in the gas phase it has the (η^5-Cp)$ZnCH_3$ structure with the central coordination [24]. The slip-sandwich structure has been found for complexes with methyl-substituted Cp ligands: (η^1-C_5Me_5)(η^5-C_5Me_5)Zn and (η^1-C_5Me_4Ph)(η^5-C_5Me_4Ph)Zn both in the gas phase [25,26] and in the crystal [27]. Evidently, the ring substituents prevent the formation of the bridging structure. In these compounds the angle between the Zn–C bond and the η^1-ring is 84°, whereas for the ordinary Zn–C σ-bond the angle is expected to be 54° (half of the tetrahedral angle).

The consideration of the spectra shows that in-plane ring vibrations in solution are represented by single bands (1416, 1380, 1112, 990 cm^{-1}). In the case of the type B structure with the non-equivalent rings, some differences in ring frequencies might be expected and the spectrum might be more complicated. Thus from this viewpoint, the type A structure with the equivalent rings seems more probable.

4.2. Skeletal vibrations

$ZnCp_2$ skeletal modes are arranged in the range 100–500 cm^{-1}. Contrary to the Cp ligand vibrations, some changes occurred in this region when passing from crystal to solution. The strong band at 358 cm^{-1} disappeared in the Raman spectrum, and two weak absorption bands at 378 and 494 cm^{-1} appeared in the IR spectrum. Evidently, it is caused by breaking of the bridging bonds. In the low-frequency part of the spectrum the bands are observed in the regions 260–360 and 600–630 cm^{-1}. The metal–ring vibrations of the majority of Cp complexes are placed in the region 300–500 cm^{-1}. Even in the spectrum of Cp_2Be which contains a very light beryllium atom the frequencies at 598 and 313 cm^{-1} are assigned to the metal–ring modes [10]. Thus we accept, that the frequencies above 600 cm^{-1} do not belong to skeletal vibrations, but most probable are related to the out-of-plane CH vibrations of the η^1-coordinated ring. Bands of similar frequencies are observed for cyclopentadiene (664 cm^{-1}) and (η^1-C_5H_5)$_2$Hg (639 cm^{-1}) [23].

We assigned the bands at 315 (IR, Raman), 344 (Raman) and 349 (IR) cm^{-1} observed in the spectra of the solution, to ZnCp vibrations. Their frequencies are closely related to the metal–ligand stretching modes for Cp_2Hg: 321 and 348 cm^{-1} [23]. However, the Cp_2Hg molecule is centrosymmetrical with two equivalent η^1-Cp rings and in this case the mutual exclusion rule is obeyed: the band at 312 cm^{-1} is observed only in the Raman spectrum and polarised, and the band at 348 cm^{-1} appears only in the IR spectrum. In the case of Cp_2Zn, the bands at 315 and 348 cm^{-1} are polarised, the first band being observed in both IR and Raman spectra. This evidences for a lower symmetry of the Cp_2Zn molecule that might be related with the non-equivalence of the two Cp rings. In the case of structure B, the molecule has the C_S symmetry and both metal–ligand vibrations belonging to the symmetry class A′ should be polarised in the Raman spectrum. The band at 315 cm^{-1} with a higher polarisation degree ($\rho = 0, 1$) should be assigned to the in-phase Zn–C mode, and the band at 344 cm^{-1} ($\rho = 0, 25$) to the out-of-phase mode.

If one of the Cp rings has η^5-coordination, besides the νM–Cp band, the tilt vibration of the Cp ring with a close frequency should appear in the spectra. For C_{5v} local symmetry of the η^5-ligand it belongs to the degenerate E class, but taking into account the C_S symmetry of the whole molecule, the degenerate band can be split. The infrared active bands at 349 and 494 cm^{-1} can be assigned to these vibrations. For the η^1-coordinated ring the corresponding vibration transforms to the deformation of the M–C–C angle (δMCC) and is expected to have a lower frequency. The band at 260 cm^{-1} in the IR spectrum can be assigned to that vibration. The band at 171 cm^{-1} lies in the range typical of bending δCpMCp vibrations. Thus, the low-frequency spectra are in accordance with the assumption that the molecule contains two non-equivalent Cp rings and has the structure of the (η^5-Cp)(η^1-Cp)Zn type (structure B).

Let us consider from that viewpoint the spectrum in the region of out-of-plane (ρCH) vibrations (600–800 cm^{-1}). Three vibrations of A_1, E_1 and E_2 classes are expected for the η^5-C_5H_5 ring with the C_{5v} local symmetry. The first two are active in IR spectra and all three are active in Raman spectra. In the Raman spectrum the ρCH bands are usually weak and the A_1 class bands are polarised. For the η^1-ligand there are five bands, with some of these vibrations having frequencies below 650 cm^{-1}. The band at 774 cm^{-1} is strong in the IR spectrum and polarised in Raman and may be assigned to ρCH(A_1). The assignment of the rest of the vibrations is controversial, since the bands at 736, 755, 715 cm^{-1} are arranged in the region where both η^5- and η^1-ligand vibrations lie. The polarised lines at 624 and 632 cm^{-1} in the Raman spectrum may also belong to the ρCH vibrations of the η^1-ligand. The weak band at 616 cm^{-1} in the Raman spectrum is arranged in the region where the χCCC out-of-plane bending mode of the η^5-ligand usually appears. The overall number of bands in the ρCH vibration region exceeds the number expected for a molecule containing only one type of Cp ligands (η^5 or η^1). This is also in agreement with the assumption that the Cp_2Zn molecule has a (η^5-Cp)(η^1-Cp)Zn slip-sandwich structure analogous to that found for penta- and tetramethyl-substituted bis-cyclopentadienylzinc complexes.

4.3. Low-temperature spectrum of the crystal

The solid state Raman spectrum at low temperature contains considerably more bands than that at room temperature (Table 1). Such an effect might be expected taking into account the narrowing of the bands with decreasing temperature, the existence of non-equivalent molecules in the crystal, and also the possibility of Davidov's band splitting (the crystal contains 8 molecules per one unit cell) [9]. However, the spectra in the region of the crystal lattice vibrations (below 150 cm^{-1}) show that the spectral changes are more essential. Thus, the strong Raman bands at 142 and 68 cm^{-1} disappear at 20 K. This evidences that the phase transition with a change in the crystal structure takes place at low temperatures.

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