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Structure and vibrational spectra of dicyclopentadienylzinc. A DFT study

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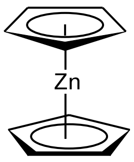
The quantum-chemical DFT calculations of the Cp_2Zn structure confirm the conclusion made earlier from the vibrational spectra that the sandwich structure $(\eta^5\text{-}C_5H_5)_2Zn$ (**A**) is not energetically favorable and more favorable are the close in energy $\pi\sigma$-structure $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Zn$ (**B**) and σ-structure $(\eta^1\text{-}C_5H_5)_2Zn$ (**C**). The vibrational spectra of structures **B** and **C** with the DFT-derived force fields were calculated. A comparison of the calculated spectra of the isolated Cp_2Zn molecules with the experimental data gives no way of deciding between the **B** and **C** structures. It is most likely that the molecule is nonrigid and experiences a strong influence from the nearest environment in solution or in the crystalline state.

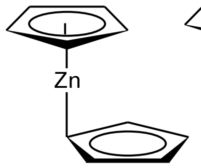
Key words: dicyclopentadienylzinc, molecular structure, vibrational spectra, density functional theory.

The vibrational spectra of the biscyclopentadienyl metal complexes Cp_2M have been studied and discussed in detail in several reviews and monographs.[1—5] The spectrum of the coordinated Cp ligand was shown to depend on the type of coordination (pentahapto η^5 or monohapto η^1) and the nature of the metal—ligand bond (ionic, central σ- or π-bond). As a rule, a study of the vibrational spectra makes it possible to establish reliably the structure of the Cp_2M complex. However, the spectroscopic characteristics of several Cp complexes, including dicyclopentadienylzinc Cp_2Zn, do not allow an unambiguous conclusion about the structure to be made.

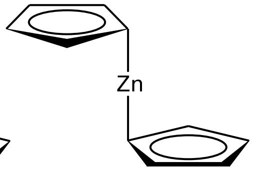
The researchers[6], who were the first to synthesize the Cp_2Zn complex, characterized it by seven absorption bands in the IR spectrum and proposed a ferrocene-like sandwich structure $(\eta^5\text{-Cp})_2Zn$ (structure **A**) for this complex. The Cp_2Zn complex was attributed[5] to typical cyclopentadienyl complexes with the C_{5v} symmetry of the Cp ligand. The ^1H NMR spectroscopic data allowed a suggestion[7] that the Cp_2M complexes (M = Zn, Cd, and Hg) have a sandwich structure with the "central σ-bond." However, the authors of Ref. 8 using the analogy with Cp_2Hg ascribed to dicyclopentadienylzinc the formula $(\eta^1\text{-Cp})_2Zn$, where the Zn atom is bound only to one C atom of the Cp ring by the ordinary σ-bond (structure **C**).



A



B



C

The X-ray diffraction study[9] of the Cp_2Zn crystal showed that the molecules in the solid state form a staggered chain of Zn atoms in which each Zn atom is linked with two bridging Cp ligands and the terminal Cp group. Assuming that the interatomic distances shorter than 2.5 Å correspond to the Zn—C bond, one has to accept that each of the Cp rings is η^2-bound to the Zn atom (bond lengths from 2.04 to 2.41 Å). However, the structure of the isolated Cp_2Zn molecule is unknown because it can substantially differ from the structure of molecules in the crystal. For example, the $(\eta^5\text{-}C_5H_5)ZnMe$ structure of the C_{5v} symmetry was shown[10] for the related CpZnMe molecule by the gas-phase electronographic method. However, the same molecule in crystal forms polymeric chains with the bridging Cp groups.[11]

We have previously studied in detail the IR spectra in the medium and long-wave regions (4000—50 cm^{-1}) and the Raman spectra of Cp_2Zn in the solid state and in solutions.[12] Analysis of the obtained spectroscopic data and comparison with the spectra of other Cp complexes suggested that the unusual structure of "slip-sandwich" $(\eta^1\text{-Cp})(\eta^5\text{-Cp})Zn$ (structure **B**) is most probable for Cp_2Zn.

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The structure **B** was found for the complexes with the 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 in both the gas phase[13,14] and crystal.[15] It is most likely that substituents in the ring prevent the formation of bridged structures. The angle between the Zn—C bond and the plane of the η^1-coordinated Cp ring is 84° in these compounds, whereas in the case of the standard σ-Zn—C bond it should be close to 54°44´ (half a tetrahedral angle).

Quantum-chemical calculations of the structure and vibrational spectra of transition metal compounds became available with the appearance of the density functional theory (DFT). In some cases, DFT calculations reproduce well vibrational spectra of transition metal compounds without the procedure of force field scaling, which is usually used in the Hartree—Fock calculations.

The presently available DFT calculations of the vibrational spectra and structure of the π-complexes of transition metals, *viz*., ferrocene (η^5-C_5H_5)$_2$Fe,[16] (η^6-benzene)chromiumtricarbonyl (η^6-C_6H_6)Cr(CO)$_3$,[17] and dibenzenechromium (η^6-C_6H_6)$_2$Cr,[17] as well as our recent calculation of (η^6-naphthalene)chromiumtricarbonyl (η^6-$C_{10}H_8$)Cr(CO)$_3$,[18] showed that the vibrational frequency are well reproduced when the calculation gives the geometric structure of a molecule with a high accuracy. Therefore, DFT approximations of a rather high level (nonlocal approximations) should be used, if possible, for optimization of the geometric parameters of molecules. The results obtained in the cited works allowed one to perform the complete interpretation of the IR and Raman spectra, to determine the force fields of molecules, and to discuss the influence of complex formation on the force constants and the character of vibrations of the metal-coordinated π-ligand.

The purpose of this work is to apply the quantum-chemical DFT method for the calculation of the structure of the isolated Cp_2Zn molecule, to study the vibrational spectra of Cp_2Zn in the gas phase, and to compare them with the experimental spectra in the solid state and solution, where the destruction of the polymeric structure characteristic of crystal can be expected.

Experimental

Quantum-chemical DFT calculations were carried out using the GAUSSIAN-98 program,[19] two different functionals BLYP and B3LYP, and different basis sets: in the DZ basis set using the LanL2 pseudo-potential[20] and in the extended 6-311G* basis set. Semiempirical AM1 calculations were also performed.

In addition, DFT calculations using the PRIRODA program[21] were carried out. The generalized gradient approximation (PBE) was used for the exchange-correlation energy.[22,23] For the expansion of one-electron functions, we used the extended atomic basis sets of grouped functions of the Gaussian type (5s1p)/[3s1p] for the H atom, (11s6p2d)/[6s3p2d] for the C atom, and (18s6p6d5f5g)/[7s5p5d] for the Zn atom. According to the algorithm,[21] to calculate the matrix elements of the Coulomb and exchange-correlation potential, we used the electron density expansion in an auxiliary basis set consisted of the sets of atom-centered nongrouped functions of the Gaussian type.

Vibrational frequencies and intensities in the IR spectra were calculated using the same programs. Vibrations were calculated in the Cartesian coordinates. The NCA99 program package was used to transform the obtained data into the system of internal coordinates.[24]

Results and Discussion

Geometric parameters. In each of the approximation used, the calculation was performed as follows. Three initial structures of the Cp_2Zn system, **A**, **B**, and **C**, were used. The local energy minimum, which is closest to the initial structure, and the global energy minimum were determined using the GAUSSIAN-98 program. The initial **A** and **C** structures, the latter with both *syn*- and *anti*-arrangement of the η^1-coordinated Cp rings, were chosen for the calculation by the PRIRODA program. The global energy minimum corresponding to the most favorable configuration was determined for all initial structures.

Some results of the calculations are presented in Table 1. Three energy minima corresponding to all of the three above structures **A**—**C** were localized by both the DFT and semiempirical AM1 methods in the LanL2DZ basis set using the GAUSSIAN-98 program. Structure **A** is always least energetically favorable. Its energy is 5—11 kcal mol^{-1} higher than that of structure **B** corresponding to the global minimum. The calculations using the PRIRODA program, regardless of configuration, also result in a global minimum corresponding to structure **B**. The differences in the Gibbs free energies (ΔG), which take into account the contribution of the entropy factor and were calculated for $T = 298.15$ K, are also presented in Table 1. The DFT calculations give the same conclusion on the relative stability of the structures that the comparison of the ΔE values. The semiempirical AM1 calculations by the ΔG value gives the more stable structure **C**, although its difference from structure **B** remains small. The geometric configurations obtained for three possible $ZnCp_2$ structures by the BLYP/LanL2DZ method are presented in Fig. 1 along with the same numeration of atoms, which is used in Table and in the text.

The number of imaginary frequencies in the calculated vibrational spectra for each form is also given in Table 1. It is seen that for structures **A** and **C**, in some cases, from one to three imaginary frequencies are present, *i.e.*, perhaps, some other extreme points rather than the true minima on the potential energy surface (PES) correspond to these structures. The absence of the imaginary vibrational frequencies for structure **B** confirms that it

Table 1. Some geometric and thermodynamic parameters of structures **A**, **B**, and **C** of the Cp_2Zn molecule calculated by the DFT method in different approximations

Parameter	AM1			Program PRIRODA[a], **B**	G98 BLYP				G98 B3LYP 6-311G*	
					LanL2DZ			6-311G*, **C**		
	A	**B**	**C**		**A**	**B**	**C**		**B**	**C**
Bond/Å										
Zn(1)—C(2)	2.347	2.345	1.955	2.207	2.408	2.291	2.120	1.984	2.199	1.990
Zn(1)—C(3)	2.347	2.247	2.847	2.263	2.407	2.445	2.561	2.678	2.361	2.455
Zn(1)—C(4)	2.349	2.348	3.748	2.337	2.405	2.571	3.077	3.395	2.416	2.984
Zn(1)—C(5)	2.350	2.346	3.744	2.332	2.405	2.510	3.078	3.395	2.296	2.984
Zn(1)—C(6)	2.348	2.344	2.837	2.255	2.407	2.338	2.562	2.678	2.154	2.455
Zn(1)—C(12)	2.345	1.944	1.955	1.990	2.408	2.081	2.120	1.984	1.961	1.990
Zn(1)—C(13)	2.347	2.839	2.851	2.672	2.407	2.735	2.561	2.678	2.698	2.456
Zn(1)—C(14)	2.351	3.755	3.750	3.398	2.405	3.442	3.077	3.396	3.453	2.985
Zn(1)—C(15)	2.351	3.760	3.742	3.398	2.405	3.442	3.078	3.396	3.453	2.984
Zn(1)—C(16)	2.347	2.849	2.834	2.673	2.407	2.737	2.562	2.678	2.698	2.456
Angle[b]/deg										
α	—	—	—	—	—	78.0	86.2	76.4[a]	86.7	89.2
β	—	—	—	—	—	17.3	2.3	9.1	2.9	27.0
C(2)—Zn—C(12)	117.5	151.8	180.0	152.2	118.4	159.4	179.9	179.9	160.3	180.0
ΔE/kcal mol^{-1}	11.21	0.00	0.51	—	5.05	0.00	0.30	—	0.00	0.95
ΔG^c/kcal mol^{-1}	10.91	0.73	0	—	5.29	0.00	0.56	—	0.00	2.76
k^d	0	0	1	0	3	0	2	0	0	2

[a] Structure **A** was taken as initial in geometry optimization.

[b] The angle between the Zn—C bond and plane of the Cp ring is α, and the angle between the planes of the Cp rings is β.

[c] Calculation for the temperature 298.15 K.

[d] The number of imaginary roots in the vibrational problem.

corresponds to the global energy minimum and agrees well with the conclusions based on the experimental study of the vibrational spectra.[12]

However, the calculations by the BLYP functional and extended 6-311G* basis set, regardless of the choice of the initial molecule configuration, converge to one global minimum corresponding to structure **C**. Two energy minima were localized by the calculation in the B3LYP/6-311G* approximation, and the deeper minimum corresponds to form **B**. The second structure with an energy by only 0.95 kcal mol^{-1} higher is close to form **C**. Two C atoms of the η^5-coordinated Cp ring are located at a closer distance from the Zn atom (2.15—2.20 Å) than three other C atoms (2.30—2.41 Å). The calculated vibrational spectrum of structure **C** contains two imaginary frequencies (see Table 1).

Thus, the results of calculations indicate unambiguously that the sandwich structure of the complex is unfa-

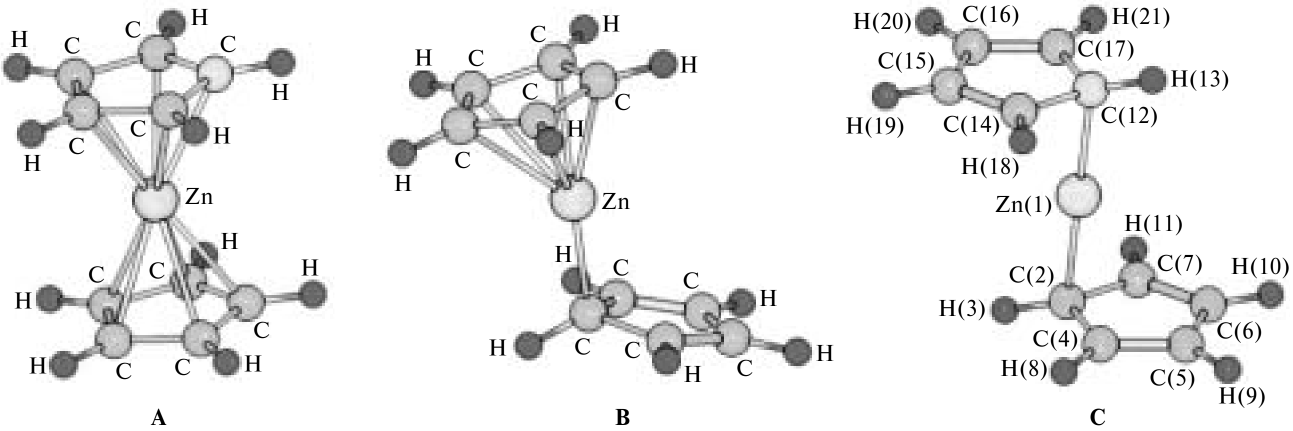

Fig. 1. Structures of the $ZnCp_2$ molecule corresponding to the energy minima in the DFT BLYP/LanL2DZ calculations: sandwich structure (**A**), "slip-sandwich" structure (**B**), and structure **C**.

vorable. However, it is difficult to choose between structures **B** and **C**. The difference in their energies is very low, and one or another structure turns out to be more favorable, depending on the choice of the basis set and approximation used. The $ZnCp_2$ molecule is likely structurally nonrigid due to the flatness of PES, which creates conditions for the easy relative movement of the Cp rings. The rings remain almost parallel. Depending on the method of calculation, the angle between the Cp rings is 2—9° for structure **C** and about 17° for structure **B**. The consequence of such a nonrigidity should be a strong dependence of the real structure of the molecule on the external conditions, *viz.*, the solvent and aggregate state.

Calculations in the extended basis set (BLYP/6-311G* SCRF=Dipole) with account for solvation effects were performed to evaluate the influence of the medium on the structure of $ZnCp_2$. The Onsager model with the following parameters was used: radius of the solute 4.56 Å and dielectric constant of the solvent $\varepsilon = 7.58$. The results do not virtually differ from those calculated in the same basis set ignoring the influence of the medium.

The calculation in the LanL2DZ basis set was performed for the $(\eta^1\text{-}Cp)_2Zn \cdot 2THF$ system. Tetrahydrofuran was chosen because $ZnCp_2$ is not dissolved in nonpolar solvents, and experiments on measuring IR and Raman spectra, which are necessary for comparison with the calculated data, were carried out in a solution of THF. As mentioned above, comparison with the spectra in the solid state is impossible because the molecules in crystal form a polymeric structure.

In the calculation, the geometry of the THF molecule was localized first, and then the optimization was performed by the position of two THF molecules in the vicinity of the $(\eta^1\text{-}Cp)_2Zn$ molecule at its unchanged geometry. The calculation showed that the THF molecules do not form a coordination bond with the Zn atom (r(Zn—O) = 4.65 Å) and poorly affect the vibrational frequency.

It seems interesting to compare the geometric parameters of the molecule for the same structure calculated in different basis sets. The metal—carbon and carbon—carbon bond lengths and some bond angles for structure **C** calculated using the GAUSSIAN-98 program in the standard LanL2DZ basis set and extended 6-311G* basis set are presented in Table 2. It is seen that the parameters obtained in calculations differ noticeably. Compared to the standard basis set, the use of the extended basis set gives the shorter Zn—C(2) and Zn—C(12) distances and somewhat longer distances between the metal atom and C atoms, which is caused by some increase in the angle between the planes of the rings (from 2.3 to 9.1°). The calculation in the 6-311G* basis set gives the shorter C(2)—C(3) and C(4)—C(5) bond lengths (1.38 Å), and the ring has a more pronounced diene structure. The B3LYP/6-311G* calculation gives shorter distances from the Zn atom to the C atoms, which are not bound to the metal, as compared to the data of the BLYP/6-311G* method.

Table 2. Metal—carbon and carbon—carbon bond lengths and some bond angles for structure **C** calculated using the GAUSSIAN-98 program in different basis sets

Parameter	BLYP/ LanL2DZ	BLYP/ 6-311G*	B3LYP/ 6-31G*
Bond/Å			
Zn—C(1) (Zn—C(12))	2.120	1.984	1.986
Zn—C(2) (Zn—C(13))	2.561	2.675	2.456
Zn—C(3) (Zn—C(14))	3.077	3.396	2.984
C(1)—C(2) (C(12)—C(13))	1.482	1.483	1.459
C(2)—C(3) (C(13)—C(14))	1.419	1.380	1.386
C(3)—C(4) (C(14)—C(15))	1.447	1.448	1.425
Angle/deg			
C(1)—Zn—C(12)	179.87	179.94	179.96
Zn—C(1)—C(2) (Zn—C(12)—C(13))	88.83	100.15	89.41
Zn—C(1)—H(7) (Zn—C(12)—H(17))	112.48	107.46	112.55
β*	2.3	9.1	27.0

* The angle between the planes of the Cp rings.

Calculation of vibrational spectra. It was primarily assumed that a comparison of the calculated and experimental data for structures **A**, **B**, and **C** suggests the structure of the $ZnCp_2$ molecule from the coincidence of the experimental frequencies with the frequencies calculated for different forms. In fact, the comparison shows that structure **A** can immediately be rejected because the experimental spectra contain much more bands than it is expected for the structure with a high symmetry (D_{5h} or D_{5d}). As for structures **B** and **C**, their spectra, which were calculated in the same BLYP/LanL2DZ approximation and manifested several noticeable differences in frequencies and intensities of the bands, do not allow the unambiguous choice to be made, because the calculation unsatisfactorily reproduces the experimental data. The use of the 6-311G* basis set results in the only stable structure **C**. However, the spectrum calculated for this structure does not either reproduce the experimental results (Table 3). This confirms, first, vibrations involving the metal atom. The frequency of symmetric vibrations of the Zn—C bond is well reproduced (calculation 327 cm^{-1}, experiment 315 cm^{-1}). The remarkable intensity of this band in the Raman spectrum and the degree of its depolarization are correctly predicted. However, the weak band in the IR spectrum corresponds to this vibrations, while according to the calculation, it should not appear in the IR spectrum. According to the calculation, the strong band in the IR spectrum at ~410 cm^{-1} should correspond to the antisymmetric stretching vibration of the Zn—C bond. However, the real IR spectrum in a region of

Table 3. Experimental and theoretical frequencies (ν) and intensities[a] (I) in the IR and Raman spectra of Cp_2Zn calculated for the most stable structure **C** in the 6-311G* basis set

Calculation				Experiment (solution in THF)		Assignment[b] (PED)
Raman		IR		Raman, ν/cm^{-1} $(\rho)^e$	IR, ν/cm^{-1}	
ν^c/cm^{-1}	I^d $(\rho)^e$	ν^c/cm^{-1}	I^d			
3138 [3089]	533 (0.14)	3138 [3089]	26	3090 m (0.1)		$100q$
3130 [3082]	48	3130 [3082]	61			$100q$
3116 [3068]	200	3116 [3068]	43		3076 w	$100q$
3105 [3058]	138	3105 [3058]	6	3063 w		$100q$
3043 [2996]	203	3043 [2996]	11			$100q$
1512	6					$82Q + 18\beta$
1412	49 (0.13)			1416 vw		$56Q + 44\beta$
		1405	62		1416 w	$56Q + 44\beta$
1379	46	1379	9	1380 vw		$51Q + 49\beta$
1102	35 (0.23)			1112 vs (0.06)		$67\beta + 33Q$
					1099 w	
1075	15	1075	11		THF[f]	$92\beta + 8Q$
1030	21 (0.06)	1029	6		1032 m	$81Q + 19\beta$
		962	16		960 w	$58Q + 42\beta$
		953	8		THF[f]	$53Q + 47\beta$
		910	340		864 s	$70\beta + 30Q$
886	225	886	9	833 w		ZnCH
842	10	842	10			$64\rho + 36\chi$
		818	7			
814	40 (0.27)			774 m (0.21)	774 vs	$85\alpha + 15\beta$
718	10	717	184	755 sh	736 s	100ρ
		663	70			$77L + 23\rho$ (χ)
639	80 (0.34)			632 m (0.20)		$72L + 28\rho$ (χ)
				624 m (0.20)	622 m	
				616 sh		
					494 w	
		410	41		378 vw	$100L$ (ν^{as})
				344 w (0.25)	349 m	
327	38 (0.15)			315 s (0.15)	315 w	$100L$ (ν^s)
		151	3		260 vw	
		132	4		171 vw	
94	13					δ(ZnCC)
62	11 (0.54)					δ(CpZnCp)

[a] The calculated frequencies of the bands, whose intensity are higher than 3 km mol^{-1} in the IR spectrum and 5 A^4/AMU in the Raman spectrum, are presented.

[b] The following designations were used: Q and q are the stretching vibrations of C—C and C—H, respectively; α and β are the bendings of the C—C—C and C—C—H angles, respectively; ρ is the nonplanar vibration of CH; χ is the nonplanar bending of the ring; and L is the stretching vibration of C(ring)—Zn.

[c] The frequencies presented in brackets were obtained using the scaling factor 0.985.

[d] The total intensity is presented for two almost coinciding calculated frequencies.

[e] The degree of depolarization is indicated in parentheses.

[f] The region of strong absorption of THF.

300—600 cm^{-1} contain no strong bands, and the closest in frequencies experimentally observed bands at 349 and 378 cm^{-1} are lowly intense. In the region of out-of-plane vibrations of the Cp rings, the CH out-of-plane vibrations, and the ZnCH bending vibrations at 600—900 cm^{-1}, the calculation poorly reproduces both the frequencies and intensities of bands in the spectra. The frequencies in a region of 950—1550 cm^{-1}, where out-of-plane Cp vibrations lie (stretching vibrations ν(CC) and bending vibrations β(CH)), are rather well reproduced. The CH stretching frequencies are overestimated because anharmonicity was ignored. However, when multiplying by the scaling factor 0.985, rather good agreement with experiment is achieved.

It should be admitted, on the whole, that, unlike other π-complexes of transition metals for which the DFT calculations are presently available,[16—18] the calculation for $ZnCp_2$ in the approximations used in this work badly reproduce the vibrational spectra.

Unsatisfactory agreement of the calculated spectra with experiment can be explained by several factors. Perhaps, the calculation insufficiently well reproduces the geometric structure of the coordination node of the molecule. This can be caused, as already mentioned, by the flattened character of the PES in the vicinity of the minimum and related nonrigidity of the structure of the molecule. The same reason can lead to the insufficient accuracy of calculation of the force coefficients and electrooptical parameters of the molecule, which determine its vibrational frequencies and intensities of bands in the IR and Raman spectra.

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