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The molecular structure of dicyclopentadienylzinc (zincocene) determined by gas electron diffraction and density functional theory calculations: η^5,η^5, η^3,η^3 or η^5,η^1 coordination of the ligand rings?

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Dedicated to professor E.O. Fischer, a pioneer in the field of organometallic chemistry who introduced one of us (A.H.) to metallocene chemistry 40 years ago

Abstract

Structure refinements to gas electron diffraction data and density functional theory calculations at the B3LYP/LanL2DZ level show that dicyclopentadienylzinc, Cp_2Zn, has an η^5,η^1 slip sandwich molecular structure in the gas phase.
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1. Introduction

The synthesis of dicyclopentadienylzinc, or zincocene, was first reported by E.O. Fischer and co-workers more than 40 years ago; reaction of $ZnCl_2$ with NaCp (Cp = cyclopentadienyl) in diethylether yielded Cp_2Zn as a colourless solid which was 'practically insoluble' in organic solvents like benzene or methylene chloride and sintered without melting at 190–200 °C [1]. The similarity of the IR spectrum of the solid to that of Cp_2Mg prompted the authors to suggest a sandwich structure similar to that of Cp_2Mg or ferrocene itself [1]. Some 10 years later Lorberth described an improved synthesis, from HCp and $Zn[N(SiMe_3)_2]_2$, Me = methyl, and showed that the ^{1}H-NMR spectrum of a saturated solution in DMF (N,N′-dimethylformamide) at room temperature consisted of one sharp line only [2]. This result was interpreted as additional evidence for a sandwich structure.

An investigation by X-ray diffraction has later shown that crystalline Cp_2Zn consists of infinite chains of Zn atoms separated by bridging Cp groups [3]. Each Zn atom is surrounded by two bridging and one terminal Cp ring. The chains contain two crystallographically independent Zn atoms arranged in the order -Zn(1)(μ-Cp)Zn(2)(μ-Cp)Zn(2)(μ-Cp)Zn(1)(μ-Cp)-. Each Zn atom is situated above the periphery of the terminal Cp ring; the interatomic distances indicate bonding interactions between Zn and two C atoms. Similarly the Cp rings bridging crystallographically independent zinc atoms appear to interact with each of them in an η^2 manner. The Cp rings bridging Zn atoms of the same type are disordered, but it seems clear that a majority— perhaps all—of the metal atoms are bonded to each of the three Cp rings in an η^2 manner.

Two derivatives of zincocene has been studied in the gas phase by electron diffraction [4]. Both were found to adopt molecular structures in which one ring was coordinated to the metal in an η^5 and the second in

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an η^1 manner. In the decamethyl derivative $(Me_5C_5)_2Zn$ the planes of the two rings are approximately parallel, in the trimethylsilyl derivative $(Me_3SiC_5H_4)_2Zn$ the angle between the ring planes could not be accurately determined, but the best fit was obtained with an angle of $37°$. Somewhat surprisingly the Zn atom and the trimethylsilyl groups appeared to be bonded to the same carbon atom in the η^1 ring [4].

A subsequent investigation of $(Me_5C_5)_2Zn$ by X-ray crystallography showed that this compound forms molecular crystals [5], perhaps because the Me_5C_5 ligand rings are too bulky for three of them to be accommodated in the coordination sphere of a Zn atom. The η^5,η^1 coordination modes observed in the gas phase are retained in the solid phase, but a more a accurate determination of the structure was thwarted by disorder of both the metal atom and the rings. An X-ray investigation of crystalline $(PhC_5Me_4)_2Zn$ (Ph = phenyl) was more successful; though the metal atom was found to be disordered, the ligands appeared to be ordered [5]. The two ligands in the molecular unit were related through an inversion centre and the C_5 rings are thus parallel by symmetry. The metal atom was disordered between two positions between the rings, in each position it is η^5 coordinated to one ring and η^1 to the other. The Zn–C bond to the η^1 ring is approximately perpendicular to the ring plane and significantly longer, (209 pm) than the single Zn–C bond in Me_2Zn (193 pm) [6]. Such η^5,η^1 structures have been commonly referred to as 'slip sandwich' structures to distinguish them from other η^5,η^1 complexes where bond distances and valence angles suggest that the metal atom is bonded to the η^1 ring through a normal two-centre σ bond to an approximately sp^3 hybridised C atom. Both the *iso*-propyl derivative $(i\text{-}Pr_4C_5H)_2Zn$ [7] and the *tert*-butyl derivative $(t\text{-}BuC_5Me_4)_2Zn$ [8] have later been found to adopt slip sandwich structures in the crystalline phase.

There is no reason to believe that C–C bond distances or CCC valence angles in the η^5 and η^1 ligands in a slipped sandwich molecule are identical. It appears probable therefore that the ligand rings are in fact disordered and that the carbon atom coordinates obtained by refinements of an ordered model represents the average of two slightly different positions. Similarly, there is no reason to believe that the ligand rings of a slip sandwich molecule are exactly parallel. The parallelism observed in the solid state may be the result of crystal packing forces, alternatively it may be due to disorder, i.e. to the supposition of two ligands with slightly different tilt angles.

Very recently Carmona and co-workers have described the crystal structure of $(Me_3SiC_5Me_4)_2Zn$ which provides the first example of a zincocene derivative which does not adopt a slip sandwich structure in the solid state [8]. This compound forms perfectly ordered molecular crystals. The structure is similar to the η^5,η^1

structure observed for $(Me_3SiC_5H_4)_2Zn$ in the gas phase [4] in so far as Zn and the trimethylsilyl group in the η^1 ring are bonded to the same C atom. The length of the $Zn–C(\eta^1)$ bond (195 pm) as well as the angle between the bond and the ring plane ($110°$) suggest that in this molecule the interaction may be described as a normal two-centre σ bond to an approximately sp^3-hybridised C atom.

Garkusha and co-workers have analysed the IR and Raman spectra of unsubstituted Cp_2Zn in both the crystalline phase and tetrahydrofurane (THF) solution, and proposed an η^5,η^1 structure in solution similar to the slip sandwich structures described above [9]. Such a structure does indeed seem very reasonable; as in the case of $(\eta^5\text{-}Cp)ZnMe$ [10] it could be taken to imply that the metal atom is surrounded by an electron octet (in addition to the 10 $3d$ electrons), while an η^5,η^5 sandwich structure would seem to imply that the metal atom is surrounded by 22 electrons. Yet some doubt remains; the metal atom in Cp_2Ge has two more valence electrons than Zn but this molecule nevertheless adopts an angular sandwich structure with two η^5 bonded rings [11]. Secondly, since the introduction of methyl and other substituents on the Cp rings in leads to a breakdown of the polymeric crystal structure of Cp_2Zn, it cannot be ruled out that the same substituents would destabilise an η^5,η^5 sandwich structure of Cp_2Zn relative to an η^5,η^1 structure. Finally, THF is a strongly coordinating solvent, and the solution structure of Cp_2Zn might be different from that of the free molecule.

The first synthesis of the dicyclopentadienyl derivative of the heaviest Group 12 element, mercury, was reported by Wilkinson and Piper in 1956 [12]. The low melting point, $83–85°C$, and good solubility in benzene and other non-coordinating solvents indicate a molecular crystal structure, and Wilkinson and Piper suggested that the metal atom is bonded to each ring through a localised single Hg–C bond. The η^1,η^1 coordination modes have since been confirmed by X-ray crystallography [13]. To the best of our knowledge CP_2Hg is the only dicyclopentadienyl metal compound which has been shown to adopt this structure.

The third and last Group 12 dicyclopentadienyl derivative, Cp_2Cd, was first synthesised by Lorberth [2]. The high melting point (about $250°C$ with decomposition) and low solubility in non-coordinating organic solvents indicate a polymeric crystal structure, presumably similar to that of the zinc analogue, but both the crystal and gas phase molecular structure remain unknown.

In this article we report the results of a structure investigation of the free Cp_2Zn molecule by gas electron diffraction (GED) and density functional theory (DFT) calculations.

2. Results and discussion

2.1. DFT calculations

Structure optimisation of a regular sandwich model with staggered ligand rings, i.e. under D_{5d} symmetry, converged to yield the bond distances listed in Table 1. Calculation of the molecular force field followed by normal coordinate analysis did, however, yield two degenerate imaginary ring slip modes of e_{1g} symmetry, showing that the optimal model of D_{5d} symmetry corresponds to a two-dimensional saddle point rather than a minimum on the potential energy hypersurface (see Fig. 1).

Table 1
Relative energies, imaginary vibrational frequencies, interatomic distances, valence angles and R-factors obtained for Cp$_2$Zn by DFT structure optimisations or by least-squares structure refinements to the GED data under D_{5d} or C_{2h} symmetry [a]

	DFT	GED
Molecular symmetry	D_{5d}	D_{5d}
Hapticity	η^5,η^5	η^5,η^5
Relative energy	+16.2	-
Imaginary frequencies	e_{1g} (108i)	-
Independent structure parameters	-	3
Independent amplitudes	-	6
Structure parameters		
Zn–C	238.4	228(2)
Zn–G [b]	204.5	193(2)
C–C	144.0	142.4(5)
C–H	108.3	110(3)
R-factor [c]		17.2%
Molecular symmetry	C_{2h}	C_{2h}
Hapticity	η^3,η^3	η^3,η^3
Relative energy	+2.8	-
Imaginary frequencies	b_u (55i)	-
Independent structure parameters	-	4
Independent amplitudes	-	6
Structure parameters		
Zn–C(1)	210.6	216(1)
Zn–C(2)	249.2	232(2)
Zn···C(3)	295.7	255(4)
C(1)–C(2)	146.8	146.0(3)
C(2)–C(3)	141.2	140.4(3)
C(3)–C(4)	143.5	142.8(3)
C–H	108.4 [d]	107(2)
∠ GC(1)H(1)	162.9	[162.9]
∠ C(5)C(1)C(2)	106.2 [e]	[106.2]
∠ GC(1)Zn	83.4	68(2)
R-factor [c]		7.8%

[a] Energies in kJ mol^{-1}, frequencies in cm^{-1}, distances in pm and angles in degree. Estimated standard deviations of GED-parameters in parentheses in units of the last digit.

[b] G = centre of gravity of Cp ring.

[c] $R = \sqrt{(\Sigma\, w(I_{obs} - I_{calc})^2 / \Sigma\, wI_{obs}^2)}$.

[d] Average value. Individual C–H distances differ by less than 0.2 pm.

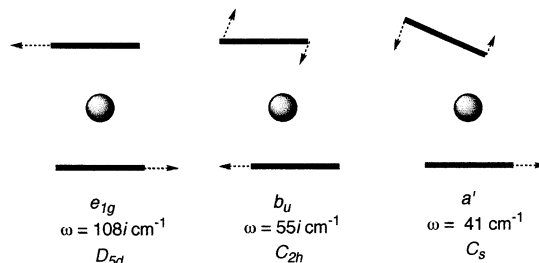[e] The other CCC angles are ∠ C(1)C(2)C(3) = 108.1 and ∠ C(2)C(3)C(4) = 108.8°.

Fig. 1. Schematic representations of imaginary vibrational modes of the D_{5d} and C_{2h} models of Cp$_2$Zn and of the lowest ring slip, ring tilt mode of the calculated equilibrium C_s structure.

Continued structure optimisation under C_{2h} symmetry yielded the slip sandwich structure shown in Fig. 2. The energy of this model is calculated to be 13.6 kJ mol^{-1} below the optimal D_{5d} model. Bond distances and valence angles are listed in Table 1. The Cp rings are essentially planar with dihedral CCCC angles less than 2°. The C(1)–H(1) bond is, however, bent some 17° out of the plane of the ring. The most noteworthy feature is the angle between the G–C(1) vector, where G is the centre of gravity of the five carbon atoms of the ring, and the C(1)–Zn bond; ∠ GC(1)Zn = 71.1°. This means that the projection of the Zn atom onto the ring plane is inside the periphery of the ring. We interpret this as evidence for Zn–C(2) and Zn–C(5) bonding and describe the rings as *trihapto* or η^3,η^3 coordinated. The Zn–C(2/5) distances which are calculated to be 20% greater than the Zn–C(1) distance are consistent with such a description. In agreement with the low symmetry of the Zn–Cp interaction C–C bond distances indicate some localisation of π-bonding in the rings.

The η^3,η^3 model is characterised by one imaginary ring slip and tilt vibrational mode of b_u symmetry which tends to change the coordination mode of one Cp ring towards η^5 and of the other towards η^1 (see Fig. 1).

Continued structure optimisation under C_s symmetry yielded the structure shown in Fig. 2. Bond distances and valence angles are listed in Table 2. The energy of the optimal C_s model is 16.2 kJ mol^{-1} below the optimal D_{5d} and 2.8 kJ mol^{-1} below the optimal η^3,η^3 model. The lower Cp ring has close to D_{5h} symmetry; the five carbon atoms are very nearly coplanar (all dihedral CCCC angles being smaller than 0.3°), the C–C bond distances differ by less than 1.2 pm and CCC valence angles by less than 0.6°. The Zn atom is situated more or less above the centre of gravity of the C_5 ring, G^5; the angle between the Zn–G^5 vector and the ring plane, ∠ ZnG^{5}C(6) is 84.4°. The five Zn–C bond distances are approximately equal corresponding to a η^5 coordination mode.

The upper ring is also essentially planar. The angle between the G^1–C(1) vector (G^1 being the centre of gravity of the five carbon atoms in the ring) and the Zn–C(1) bond, ∠ G^{1}C(1)Zn, is 103.5°, which places the
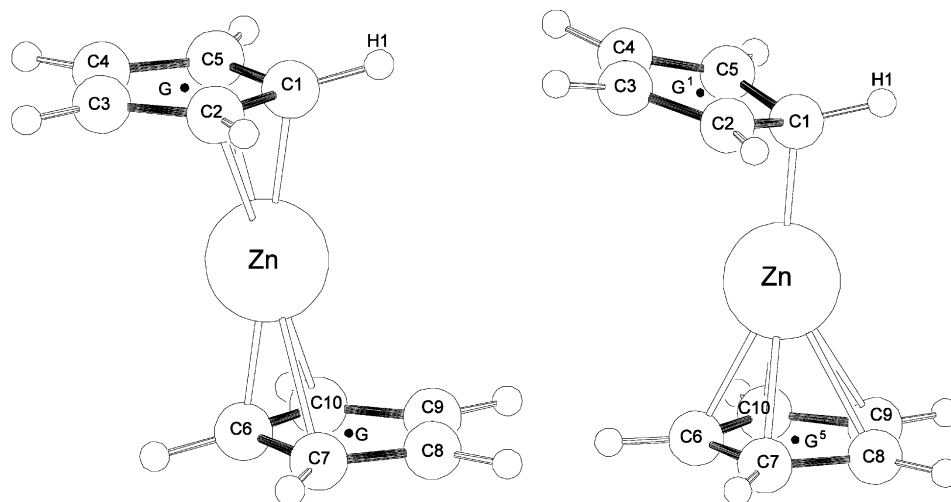
Fig. 2. Molecular models of Cp$_2$Zn. Left C_{2h}, right C_s symmetry. Program PLUTON [31].

projection of the metal atom onto the ring plane *outside* the ring periphery. The Zn···C(2) and Zn···C(3) distances are more than 30% longer than the Zn–C(1) bond distance and we describe this ring as η^1 coordinated. The calculated C–C bond distances, C(1)–C(2) = 148, C(2)–C(3) = 139 and C(3)–C(4) = 145 pm, indicate that π-bonding is less localised than in the parent hydrocarbon cyclopentadiene [14], but more localised than in the η^3,η^3 model.

All vibrational frequencies of the η^5,η^1 model are real, indicating that this structure corresponds to a minimum on the potential energy hypersurface at the B3LYP/LanL2DZ level [15]. The molecule is, however, very flexible. The lowest vibrational mode at $\omega = 10$ cm^{-1}, has a'' symmetry and may be described as one in which the two rings undergo internal rotation in opposite directions, each about its centre of gravity. The second lowest mode at 41 cm^{-1} which has a' symmetry, is a ring tilt and slip mode which distorts the structure in the direction leading to exchange of the coordination modes of the two rings; $\eta^5,\eta^1 \rightarrow \eta^1,\eta^5$ (see Fig. 1). This exchange presumably occurs via a transition state of C_{2h} symmetry, which we have calculated to lie just 2.8 kJ mol^{-1} above the equilibrium structure. The activation energy for exchange of ring coordination modes is thus of the same order as the thermal energy at the temperature of the electron diffraction experiment, RT = 3.1 kJ mol^{-1}, The combination of the a'' ring rotation mode with the a' ring slip and tilt mode would, of course, render the protons NMR equivalent, the calculated C_s equilibrium structure is thus consistent with the reported ^{1}H-NMR spectrum [2].

While this manuscript was in preparation, three groups published contradictory results of DFT structure optimisations of Cp$_2$Zn; optimisations with the B3LYP functional, a LanL2DZ basis for Zn and a 3-21G basis for C and H [16], or with the BLYP functional and a 6-311G* basis on all atoms [17] yielded η^3,η^3 equilibrium structures of C_{2h} symmetry, while optimisations with the BP86 functional, a relativistic 20 VE ECP basis for Zn and 6-31G* basis for C and H [18], or at the BLYP/LanL2DZ or B3LYP/6-311G* levels [17] yielded η^5,η^1 equilibrium structures of C_s symmetry. It is clear that the energy difference between the two forms is too small to allow the equilibrium structure to be settled by calculations alone.

2.2. Gas electron diffraction structure refinement

Our DFT calculations indicate that the D_{5d} model of Cp$_2$Zn corresponds to a saddle point rather than a minimum on the potential energy surface, and the energy of the optimised D_{5d} model ($\Delta E = 16.2$ kJ mol^{-1}) is so much higher than that of the optimised C_s model that an equilibrium structure of D_{5d} symmetry may be ruled out on the basis of the calculations alone. Least squares refinement of a molecular model of D_{5d} symmetry to the gas electron diffraction data yielded the structure parameters listed in Table 1 The R-factor is so large, $R = 17.2\%$ compared to $R = 4.7\%$ for the best C_s model, that the D_{5d} model also can be ruled out as incompatible with the GED data.

Since one cannot rule out an equilibrium structure of C_{2h} symmetry on the basis of the calculations alone, it is important that the GED structure refinements of the C_{2h} and C_s models are carried out in such a manner that statistical tests may be used to compare the goodness of fit. Structure refinements of the C_{2h} model involved the variation of four independent structure parameters, *viz.* the mean C–H and C–C bond distances, the Zn–C(1) bond distance and the angle between the Zn–C(1) bond and the ring plane, $\angle$ GC(1)Zn. All other structure parameters were fixed at calculated values. Six ampli-

Table 2
Relative energy, interatomic distances, valence angles and R-factor obtained for Cp$_2$Zn by DFT structure optimisations or by least-squares structure refinements to the GED data under C_s symmetry [a]

	DFT	GED
Molecular symmetry	C_s	C_s
Hapticity	η^5,η^1	η^5,η^1
Relative energy	0	-
Imaginary frequencies	None	-
Independent structure parameters	-	7
Independent amplitudes	-	6
Structure parameters		
The η^1 ring:		
Zn–C(1)	206.0	210(3)
Zn$\cdots$C(2)	270.4	260(3)
Zn$\cdots$C(3)	339.6	320(7)
C(1)–C(2)	148.2	147.4(3)
C(2)–C(3)	139.2	138.4(3)
C(3)–C(4)	144.8	144.0(3)
C(1)–H(1)	109.1	108(2)
C–H	108.6 [b]	108(2)
∠C(5)C(1)C(2)	105.1 [c]	[105.1]
∠G^{1}C(1)H(l)	148.7	[148.7]
∠G^{1}C(1)Zn	103.2	95(4)
The η^5 ring:		
Zn–C(6)	228.8	217(6)
Zn–C(7)	236.1	223(3)
Zn–C(8)	246.9	233(4)
Zn–G^5	205.3	190(3)
C–C	144.0 [d]	143.7(3)
C–H	108.3 [e]	108(2)
∠CCC	108.0 [f]	[108.0]
∠ZnC^{5}C(6)	84.4	85(3)
∠G^{5}ZnC(1)	170.3 [g]	187(6) [h]
R-factor [i]		4.7%

[a] Energies in kJ mol^{-1}, frequencies in cm^{-1}, distances in pm and angles in degree. Estimated standard deviations of GED-parameters in parentheses in units of the last digit.

[b] Average value of C(2)–H = 108.7 and C(3)–H = 108.4 pm.

[c] The other CCC angles are ∠C(1)C(2)C(3) = 108.4 and ∠C(2)C(3)C(4) = 109.0°.

[d] Average value. Individual C–C distances differ by less than 0.8 pm.

[e] Average value. Individual C–H distances differ by less than 0.1 pm.

[f] Average value. Individual CCC angles differ by less than 0.5°.

[g] The dihedral angle ϕ(C(6)G^{5}ZnC(1)) = 180°.

[h] The dihedral angle ϕ(C(6)G^{5}ZnC(1)) = 0°.

[i] $R = \sqrt{(\Sigma\, w(I_{obs} - I_{calc})^2 / \Sigma\, wI_{obs}^2)}$.

tude parameters were refined (see Section 3), while non-refined amplitudes were fixed at calculated values.

Structure refinements of the C_s model involved the variation of seven independent structure parameters. In addition to the four parameters used to describe the C_{2h} model, we also refined the distance from the Zn atom to the centre of gravity of the η^5 ring, Zn–G^5, the angle ∠ZnG^{5}C(6) and the angle ∠G^{5}ZnC(1). Six amplitude parameters selected in the same way as for the C_{2h} model were also refined, non-refined amplitudes were fixed at calculated values.

The best values obtained for structure parameters of the two models are listed in Tables 1 and 2. Experimental and calculated intensity curves for the two models are compared in Fig. 3. It is seen that while the C_s model leads to good overall fit between experimental and calculated intensities, the difference curves for the C_{2h} model contain ripples that cannot be removed by adjustment of the background. Experimental and calculated radial distribution curves for each model are compared in Fig. 4. While the C_s model leads to good overall agreement, the C_{2h} model fails to reproduce the peak at about 340 pm which in the C_s model is assigned to the Zn$\cdots$C(3) and Zn$\cdots$C(4) distances, and the much smaller peak at about 420 pm which in the C_s model is assigned to five approximately equal distances from C(1) to the five C atoms in the η^5 ring. The R-factors obtained in the two refinements, 7.8 and 4.7% correspond to an R-factor ratio of 1.66. The use of Hamilton's R-factor ratio test shows that the C_{2h} model may be rejected at the 99.5% confidence level [19]. Thus both calculations and experiment indicate that the equilibrium structure of Cp$_2$Zn has C_s symmetry.

The symmetry of the C_s model is low, many distance peaks overlap in the radial distribution curve, and due to the softness of the potential energy hypersurface many vibrational amplitudes are very large. The structure parameters obtained by least-squares calculations to the GED data are therefore accompanied by large uncertainties; the error limits (= 3 esd's) associated with the Zn–C(l) bond distance and the Zn to η^5 ring distance Zn–G^5 are nearly 10 pm, the error limits associated with the angles determining the positions of the rings relative to the metal atom, i.e. ∠G^{1}C(1)Zn and ∠ZnG^{5}C(6), are about 10°, and the error limit of the angle determining the positions of the ligand rings relative to each other, ∠G^{5}ZnC(1), about 15°. We
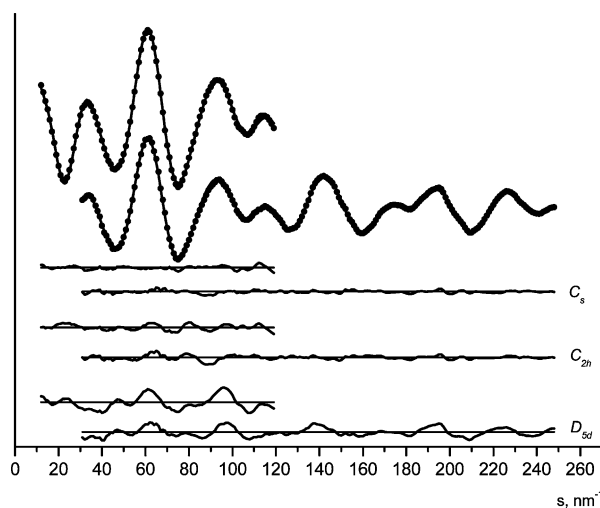

Fig. 3. Above: experimental (dots) and calculated (line) molecular intensity curves, $sM(s)$, for Cp$_2$Zn symmetry C_s. Below: difference curves for C_s, C_{2h} and D_{5d} symmetry.
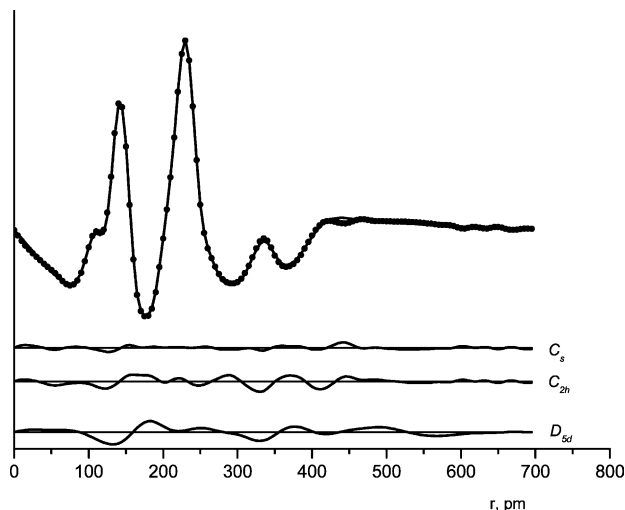
Fig. 4. Above: experimental (dots) and calculated (line) radial distribution curves for Cp_2Zn, symmetry C_s. Below: difference curves for C_s, C_{2h} and D_{5d} symmetry. Artificial damping constant, $k = 37$ pm^2.

have seen that the location of the minimum on a very flat potential energy hypersurface by DFT calculations is very sensitive to changes in the density functional or basis set. Finally, while the calculations yield an equilibrium structure, the GED structure parameters are averaged over all the vibrational states that are populated at the temperature of the experiment. All these things considered, we feel that the agreement between the DFT and the GED structure is as good as can be expected.

2.3. Concluding remarks

The gas electron diffraction results confirm that the Zn–C(1) bond is significantly longer than expected for a normal two-centre σ Zn–C bond (ca. 194 pm) and that the angle $\angle G^1C(1)Zn$ is significantly smaller than expected for an sp^3-hybridised C(1) atom (ca. 120°). We believe therefore that the structure is best described as a slip sandwich.

The structure adopted by the free Cp_2Zn molecule is thus closer to that beralloccne, Cp_2Be, than to that of any other metal dicyclopentadienyl compound [20]. But if the structures are similar, the reasons why they are adopted may still be different. The η^5,η^1 structure of Cp_2Be is commonly assumed to be due to excessive steric repulsion (i.e. antibonding) between the two rings in a regular sandwich structure: because of the small size of the metal atom the distance between the rings would be much smaller than the van der Waals thickness of an aromatic ring [21]. The Zn atom is much larger, the distance between the rings in the optimised D_{5d} model of Cp_2Zn is larger than the van der Waals thickness. As mentioned in the introduction, a D_{5d} structure of Cp_2Zn would seem to imply that the metal atom is surrounded

by 22 valence electrons, four more than the metal atom in Cp_2Fe and two more than in Cp_2Ni. The four excess electrons would be expected to enter strongly antibonding molecular orbitals obtained by combination of the $3d_{xz}$ or $3d_{yz}$ atomic orbitals of the metal atom and e_1 π-orbitals of the two rings [22]. This expectation was confirmed by the calculations on the D_{5d} model. We suggest, therefore, that the η^5,η^1 equilibrium structure is due to the destabilisation of the D_{5d} model by antibonding interactions between the metal atom and the two rings.

3. Experimental

3.1. Density functional theory calculations

DFT calculations on Cp_2Zn were carried out using the GAUSSIAN program system with the B3LYP functional and standard LanL2DZ basis sets [23]. The molecular structure was optimised and the force fields and vibrational frequencies calculated under D_{5d}, C_{2h} and C_s symmetry. The molecular force fields of the C_{2h} and C_s models were transferred to the ASYM40 program [24] for calculation of root-mean-square vibrational amplitudes, l, at the temperature of the electron diffraction experiment. The contributions from the imaginary b_u vibrational mode of the C_{2h} model were not included.

3.2. Gas electron diffraction

The sample of Cp_2Zn was synthesised and characterised as described in [9]. Synchronous GED and mass spectrometric experiments were carried out on the modified EMR-100/ADPM-1 unit in Ivanovo [25]. The sample was evaporated from a graphite effusion cell with a cylindrical nozzle of length 1.2 and diameter 0.6 mm. The nozzle temperature was about 102 ± 5 °C corresponding to a vapour pressure of about 0.05 torr. The vapor composition was monitored by MS. The most intensive peaks were Cp_2Zn^+, $CpZn^+$ and Zn^+; no peaks corresponding to ions of greater mass than the parent indicated the presence of associated species. Exposures were made with nozzle-to-plate distances of about 60 and 34 cm. Optical densities of three photographic plates for each distance were measured by a modified MD-100 (Carl Zeiss, Jena) microdensitometer [26]. The electron wavelength was calibrated using the diffraction pattern from ZnO powder.

The background functions, $G(s)$, were refined by Fourier spectrum analysis of the total intensity curve $I_{obs}(s)$. The final molecular intensities

$$sM(s) = [I_{obs}(s)/G(s) - 1]s$$

covered the ranges 12–119 nm^{-1} (60 cm) and 31–248 nm^{-1} (34 cm) in steps of $\Delta s = 1$ nm^{-1}.

3.3. Structure refinements

Structure refinements by least-squares calculations on the molecular intensities were carried out using a modified version the KCED 26 program [27]. Atomic scattering factors were taken from [28]. The calculated intensity contained terms for all interatomic distances except nonbonded H···H distances. Since the refinements were carried out with diagonal weight matrices, the estimated standard deviations listed in Tables 1–3 have been multiplied by a factor of 2.5 to include uncertainty due to data correlation [29] and expanded to include a scale uncertainty of 0.2%. Since the value obtained for the angle $\angle$ G^{5}ZnC(1) was found to be particularly sensitive to the values assigned to non-refined amplitude parameters, the estimated standard deviation of this parameter has been multiplied with a factor of 3.5.

Structure refinements of Cp$_2$Zn were carried out on a regular sandwich model of D_{5d} symmetry, a slip sandwich model of C_{2h} symmetry and a C_s symmetry model.

The structure of the D_{5d} model was described by three independent parameters, *viz.* the C–H, C–C and Zn–C bond distances. In addition we refined six root-mean-square amplitudes of vibration, *viz.* the amplitudes associated with the three bond distances, with the nonbonding Zn···H distances, with the infra-ring C···C nonbonded distance at about 230 pm, and finally the average of the three inter-ring C···C distances. The start values for the latter were taken from the Hedbergs' refinement of Cp$_2$Ni [30].

The C_{2h} model was described by four independent structure parameters, *viz.* the mean C–H and C–C bond distances, the Zn–C(1) bond distance and the angle $\angle$

GC(1)Zn (see Fig. 2). The difference between individual C–H or C–C bond distances were fixed at the calculated values. So were the CCC valence angles in the rings. In the input calculated values were assigned to all amplitudes and six vibrational parameters were refined:

i)   the mean amplitude of all C–H bond distances;
ii) the mean amplitude of all C–C bond distances;
iii) the mean amplitude of all infra-ring C···C distances at about 230 pm;
iv) the mean amplitudes of all inter-ring C···C distances;
v)   the mean amplitude of the bonded Zn–C distances, *viz.* Zn–C(1) and Zn–C(2/5); and
vi) the mean amplitude of the nonbonded Zn···C(3/4) distances.

The C_s model was described by seven independent structure parameters, *viz.* the mean C–H and C–C bond distances, the Zn–C(1) bond distance and the angle $\angle$ G^{1}C(1)Zn. In addition we refined two parameters which determine the coordination geometry of the η^5 ring, namely the Zn–G^5 distance, the $\angle$ ZnG^{5}C(6) angle, and finally one angle $\angle$ G^{5}ZnC(1) which determines the relative positions of the two rings. The difference between individual C–H or C–C bond distances were fixed at the calculated values. So were the CCC valence angles in both rings. In the input calculated values were assigned to all amplitudes. Mean C–H, C–C and C···C amplitudes were refined as indicated in points (i) to (iv) above. In addition we refined: (v) the mean amplitude of the bonded Zn–C distances, Zn–C(1), Zn–C(6), Zn–C(7) and Zn–C(8); and (vi) the mean amplitude of the nonbonded Zn···C(2) and Zn···C(3) distances. Calculated and experimental vibrational amplitude parameters for the C_s model are compared in Table 3.

Table 3
Vibrational amplitudes (in pm) calculated from the DFT force field of the C_s model of Cp$_2$Zn and average amplitudes obtained by least-squares refinement to the GED data.

	DFT		GED
	Range	Average	Average
Bond distances			
Zn–C [a]	6.6–22.4	18.0	20.9(7)
C–C	4.5–5.1	4.8	5.3(3)
C–H	7.5–7.6	7.5	7.7(6)
Nonbonded distances			
Zn···C [b]	18.3–24.4	21.4	25(4)
C···C (intra Cp)	5.3–5.4	5.3	4.3(3)
C···C (inter Cp)	12.6–76.0	42.5	45(5)

[a] Zn–C(1), Zn–C(6), Zn–C(7) and Zn–C(8).
[b] Zn···C(2) and Zn···C(3).

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