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Geometry and electronic structure of bis(tetrahydridoborato)bis(cyclopentadienyl)zirconium(IV)

Bálint Sztáray [a], Edina Rosta [a], Zsolt Böcskey [b], László Szepes [a,*]

[a] *Department of General and Inorganic Chemistry, Eötvös Loránd University, PO Box 32, 1518 Budapest 112, Hungary*
[b] *Department of Theoretical Chemistry, Eötvös Loránd University, PO Box 32, 1518 Budapest 112, Hungary*

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Abstract

The geometry and the electronic structure of the title compound was investigated by UV photoelectron spectroscopy, X-ray diffraction and ab initio quantum-chemical methods. The photoelectron spectrum was recorded both at He(I) and He(II) photon energies, which was assigned on the basis of the quantum-chemical calculations and comparison with analogous complexes. Full geometry optimization was performed at the Hartree–Fock and at the second-order many-body perturbation levels of theory. The obtained geometry is in good agreement with the anticipated bidentate ligation of the BH_4 groups. The measured Zr–B distance from the X-ray studies provides further evidence for the above mentioned bonding mode of the tetrahydridoborato ligands. The ionization energies of the complex were calculated using the outer valence Green's function method. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Tetrahydridoborato ligand; He(I)/He(II) photoelectron spectroscopy; X-ray diffraction; Ab initio quantum-chemical methods

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1. Introduction

Bis(tetrahydridoborato)bis(cyclopentadienyl)zirconium(IV) belongs to the transition metal tetrahydridoborates which recently have attracted much attention [1–6]. From a practical point of view, the derivatives of the compounds are ideal precursors for chemical vapor deposition (CVD) of metal carbide, metal boride and carbide–boride hard coatings [7–10]. They are also ideal catalysts and stereoselective reducing agents of organic compounds [11–16].

Theoretical interest has focused on the mode of bonding between the metal center and the tetrahydridoborate group. This ligation may be attained via one, two and three hydrogen bridges [17–20]. The bonding through only one hydrogen–metal bond as well as mixed haptocity occurs quite rarely [3]. Reviews of bonding studies on metal borohydride complexes are available in the literature [17,21–24]. It can be generally stated that the electronic structure of the metal center plays the most important role in the ligation and the 18-electron rule can be applied in several cases. Other important factors are the sizes of the metal ion and the other ligands.

The main difficulty for which it is hard to determine whether there are bi- or tridentate BH_4 ligands is that the hydrogen atoms are often not visible for diffraction techniques and they are very fluxional compared to the NMR timescale [25].

IR spectroscopy proved to be the most efficient gas phase method to predict the geometry but it provides only indirect evidence and can not usually give quantitative data concerning the molecular structure. Neutron diffraction would be the most useful method for determining the whole geometry but it is not easily available.

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* Corresponding author.

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X-ray diffraction measurements generally provide data only for the boron–metal distance. Bernstein et al. proposed a method based on the theory of isolobality [22,23,26] to predict the mode of the ligation from these data. According to this idea one can assign an ionic radius to the bidentate borohydride group and an other to the tridentate. Knowing the ionic radius of the metal center and the metal boron bond length we can obtain a radius for the borohydride anion [17].

Recently these geometrical questions were made timely again because more exact quantum-chemical calculations can be performed much faster in order to help the interpretation of the experimental data.

In the literature dealing with the title compound no exact geometrical data can be found. X-ray or electron diffraction measurements have not been carried out. By comparing the IR spectra of $(C_5H_5)_2Zr(BH_4)_2$ and $(C_5H_5)_2Zr(BD_4)_2$, the two bridged structure is the most likely [27]. The electronic structure of the title compound has also been investigated but the assignment of the published He(I) photoelectron spectrum was only tentative because of the lack of quantum-chemical calculations [28].

2. Experimental

2.1. Preparation

$Cp_2Zr(BH_4)_2$ was prepared from $LiBH_4$ and Cp_2ZrCl_2 by a modified method of Nanda and Wallbridge [29]. Identity and purity were checked by GC MS.

2.2. UPS measurements

He(I) and He(II) photoelectron spectra were recorded on an ATOMKI ESA 32 instrument. The spectrometer has been described elsewhere [30]. The spectrometer has been recently equipped with a Leybold–Heraeus UVS 10/35 high-intensity gas-discharge photon source. With this lamp in He(I) mode the typical count rate on the Ar $^2P_{3/2}$ peak was higher than 200 000 cps with a FWHM of 30 meV. The sample was introduced into the ionization chamber via a direct sample inlet probe heated to 200 and 220°C at the He(I) and He(II) measurements, respectively. The spectra were calibrated using argon as internal standard. Maximum error in ionization energies is estimated to be less than 0.05 eV.

2.3. X-ray crystal structure determination

Low-quality crystal did not allow high-quality structure determination of the compound. However, the data allow important conclusions to be drawn.

Crystals of $C_{10}H_{18}B_2Zr$ ($M_w = 251.08$) are monoclinic; space group $C2/c$, $a = 14.57(2)$ Å, $b = 6.78(3)$ Å, $c = 13.36(5)$ Å, $\beta = 114.90(6)°$, $V = 1198(6)$ Å^3, $Z = 4$, $D_{calc.} = 1.393$ g cm^{-3}, $\mu = 7.112$ mm^{-1}. X-ray data were collected at room temperature from a transparent plate crystal with approximate dimensions of $1.0 \times 0.7 \times 0.5$ mm^3 by a Rigaku AFC6S diffractometer using graphite monochromated Cu–K$_\alpha$ radiation ($\lambda = 1.54178$ Å with theta range of 6.70–75.04°). Intensities were corrected for absorption by the psi-scan method. The structure was solved by direct methods and nonhydrogen atoms were refined anisotropically. A total of 62 variables were refined against 1166 observations to a final $R = 0.1031$ ($I > 2\sigma(I)$), $wR_2 = 0.2815$. Initial calculations were done using the TEXSAN package [31], the hydrogen positions were generated, and the final structure refinement calculations were carried out with SHELXL-93 [32]. The obtained atomic coordinates with the equivalent isotropic displacement parameters are given in Table 1.

2.4. Computational details

The calculations have been performed at the restricted Hartree–Fock level using Biosym's Turbomole v235 [33]. In order to include the effect of electron correlation, second order many-body perturbation theory (MBPT(2), also referred to as MP2) calculations were also carried out using the Gaussian 94 package [34]. We have used the dzp basis set of Ahlrichs et al. [35] for the boron, carbon and the hydrogen atoms. For the zirconium atom the averaged relativistic effective potentials (AREP) of LaJohn and coworkers [36] with polarized double zeta valence basis functions were applied. Full geometry optimizations were performed in natural internal coordinates with Turbomole and in redundant internal coordinates with Gaussian. The natural coordinates describing the ring systems were defined the usual way using Fogarasi's INTC program [37,38]. The relative position of the Cp rings and the tetrahydridoborato ligands were defined by manually determined natural internal coordinates [39].

Table 1
Atomic coordinates ($\times 10^4$ Å) and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for the title compound [a]

	x	y	z	U_{eq}
Zr(1)	0	49(1)	2500	45(1)
C(1)	1167(10)	−2634(28)	3434(22)	122(8)
C(2)	1203(9)	−2408(27)	2425(18)	115(7)
C(3)	1670(13)	−620(37)	2440(2)	105(6)
C(4)	1867(17)	210(32)	3410(43)	126(14)
C(5)	1598(13)	−1007(48)	4037(16)	119(6)
B(1)	−42(17)	2415(21)	963(13)	104(6)

[a] U_{eq} is defined as one third of the ortogonalized U_{ij} tensor.

The calculation of ionization energies can be performed at several levels. According to Koopmans' theorem [40], the ionization energies are given by the orbital energies from simple Hartree–Fock calculations. If orbital relaxation and electron correlation effects are considered to be important, higher level calculations are necessary for adequate accuracy. In the present work we used the outer valence Green's function (OVGF) method of Cederbaum and co-workers [41]. This method has been applied to several molecules [42] and has been proven to be accurate to 0.2–0.3 meV. This method has a close connection to linear response theory, and equation-of-motion methods. For the treatment of linear response we refer to review papers by Oddershede et al. [43,44]. The relation of the equation-of-motion ionization potential coupled-cluster singles and doubles (EOMI-CCSD), also known as coupled-cluster Green's function (CCGF) method to the OVGF method used in this paper was discussed in detail by Nooijen and Snijders [45]. Here we just mention that the necessary infinite-order summation is performed in OVGF by solving Dyson's equation, while in EOM-CCSD the coupled-cluster equations are used. We have recently applied the latter method for the assignment of the photoelectron spectrum of an organoarsenic compound with sufficient accuracy [46]. However, this is more expensive than the OVGF method and in the present paper—due to computational limitations—we were unable to apply it.

The approximate C_2 symmetry of the molecule was utilized in the calculations. It is clear that the first set of calculations starting from a tridentate structure contained no symmetry constraint. However, to be able to carry out the expensive correlated MBPT(2) geometry optimizations, the C_2 symmetry was utilized until convergence was reached. The final optimizations were carried out with no symmetry constraint, yielding the final geometries quite close to the anticipated C_2 symmetry.

The calculations were mostly carried out on an IBM RS/6000 model 580 computer.

3. Results and discussion

3.1. Molecular geometry

The crystal structure of the title compound was determined to gain information on the stereostructure of the compound with practical emphasis on the B–H...Zr hydrogen bridge. The asymmetric unit contains only one cyclopentadienate and one tetrahydridoborate anion along with half a Zr(IV) atom. The remaining half of the structure is generated by a crystallographic 2-fold axis. The Zr atom is coordinated in a tetrahedral fashion by two cyclopentadienyl and two tetrahydridoborate anions in the corners of a distorted tetrahedron (Figs. 1 and 2).

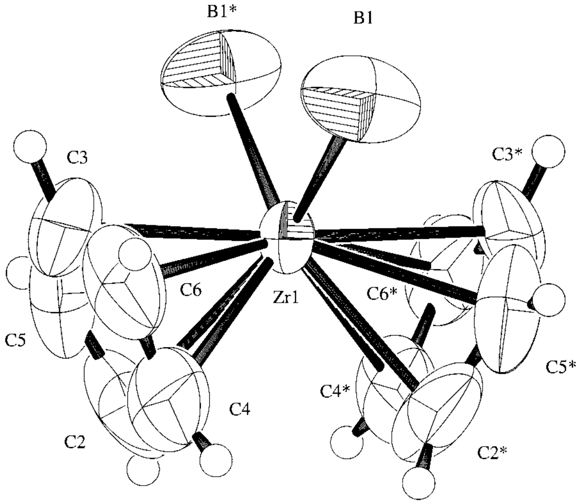

Fig. 1. Molecular structure of $Cp_2Zr(BH_4)_2$ in the crystal.

Although hydrogen atoms around the boron atom were not found from difference Fourier calculations due to the low data quality, the Zr...B distance is characteristic of the doubly bridged structures. A search of the literature has shown that for structures containing tridentate bridging, the Zr...B distance is around 2.36 Å, while for those which contain bidentate bridging the corresponding distance is around 2.58 Å [17,20]. The difference looks significant, and in the case of our structure the measured Zr...B distance is very close to the average produced by the compounds containing the bidentate bridging. An outline of the experimental geometrical parameters is given in Table 2.

Full geometry optimization was performed at the ab initio Hartree–Fock and MBPT(2) levels of theory. In the initial geometry the tetrahydridoborate groups were

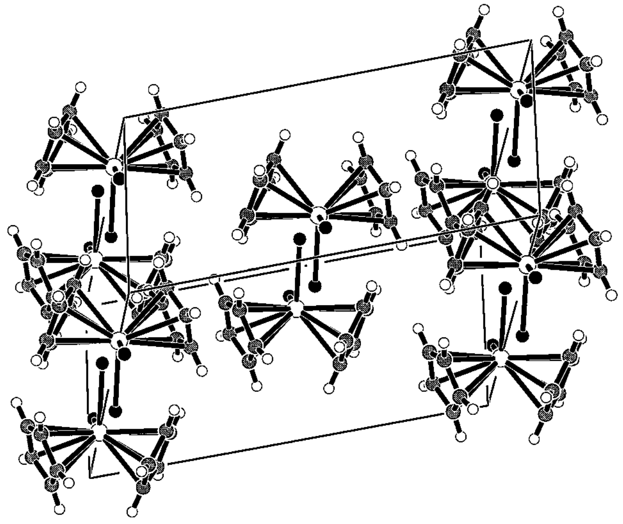

Fig. 2. Crystal packing diagram.

Table 2
Selected bond lengths (Å), angles (°) for $Cp_2Zr(BH_4)_2$ [a]

Bond lengths (Å)	
Zr(1)–C(1)	2.445(13)
Zr(1)–C(2)	2.451(13)
Zr(1)–C(4)	2.47(2)
Zr(1)–C(5)	2.48(2)
Zr(1)–C(3)	2.51(2)
Zr(1)–B(1)	2.59(2)
Bond angles (°)	
B(1)–Zr(1)–B(1) # 1	103.3(7)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x$, y, $-z+1/2$.

defined as three-bridged ligands. The optimized geometry shows, however, a two-bridged structure. This indicates that the three-bridged configuration probably does not correspond to a minimum on the potential energy surface. The optimized geometry of the molecule is shown in Fig. 3, the most important calculated bond lengths and the B–Zr–B angle are given in Table 3. The Hartree–Fock computed bond lengths are somewhat longer than the experimental distances obtained from X-ray diffraction, but this is not surprising at this level of theory. The inclusion of electron correlation significantly improves the values. This is crucial in the case of the Zr–B distance where the MBPT(2) result is in very good agreement with the measurements. This might be another confirmation of the two-bridged structure of the complex. The calculated B–Zr–B angle is substantially larger than the experimental value in both cases, but this can be due to the difference between the solid-state and the gas-phase geometry also.

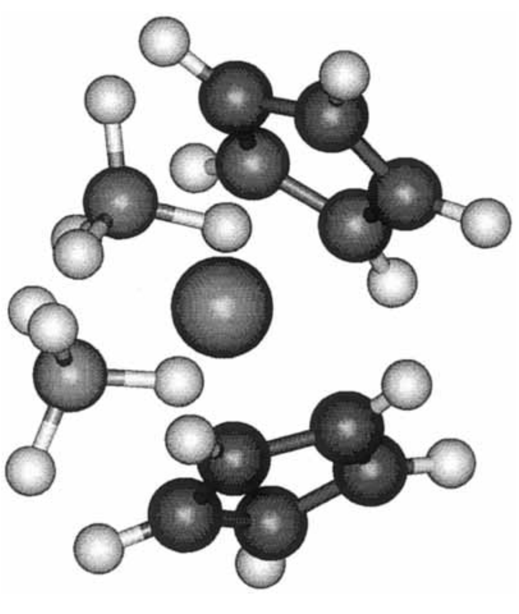

Fig. 3. The calculated ab initio molecular structure.

Table 3
Selected calculated geometrical parameters of the title compound (in Ångstroms and degrees)

	Hartree–Fock	MBPT(2)
r(Zr–C)	2.539–2.588	2.494–2.530
r(Zr–B)	2.651	2.587
r(Zr–H)	2.091, 2.169	2.066, 2.098
r(C–C)	1.400–1.416	1.414–1.427
r(C–H)	1.075–1.077	1.086–1.088
r(B–H)	1.209 [a], 1.258 [b], 1.271 [b]	1.211 [a], 1.259 [b], 1.265 [b]
∠(B–Zr–B)	112.07	111.18

[a] Terminal hydrogen.

[b] Bridging hydrogen.

3.2. Photoelectron spectra and molecular orbital calculations

The He(I) and He(II) photoelectron (PE) spectra of $Cp_2Zr(BH_4)_2$ are shown in Fig. 4. The spectra contain four broad envelops each composed of a series of overlapping peaks as demonstrated later in connection with the molecular orbital (MO) calculations. The first band (A) centered at about 9 eV possesses two maxima

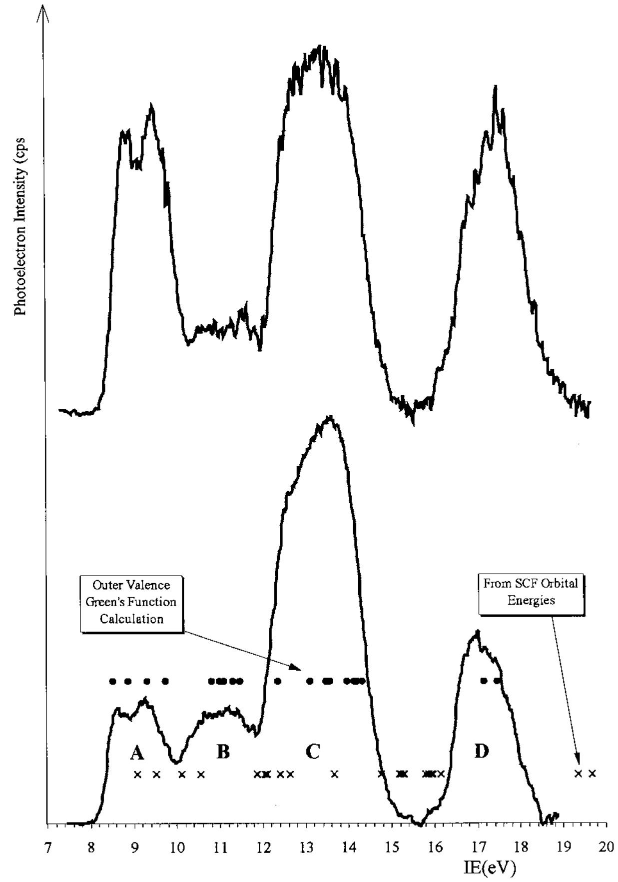

Fig. 4. The photoelectron spectrum of the complex at He(I) photon energy (lower) and at He(II) photon energy (upper) with the calculated ionization energies.

Table 4
The calculated molecular orbital energies and the corresponding orbital characters

Orbital group	HF orbital energies (eV)	OVGF ionization energies (eV)	Orbital character
A′	−9.075	8.519	Cyclopentadienyl orbital
	−9.523	8.868	Cp–Zr bond with small d-character
	−10.105	9.307	Cp–Zr bond with substantial d-character
	−10.545	9.735	Cp–Zr bond with substantial d-character
B′	−11.859	10.809	BH_4–Zr bond with d-character
	−12.053	10.990	BH_4 orbital
	−12.098	11.081	BH_4 orbital
	−12.398	11.292	BH_4–Zr bond
	−12.629	11.473	BH_4–Zr bond
C′	−13.657	12.353	Cp–Zr bond
	−14.772	13.105	Cp–Zr bond
	−15.188	13.471	Cyclopentadienyl orbital
	−15.198	13.482	Cyclopentadienyl orbital
	−15.279	13.548	Cyclopentadienyl orbital
	−15.294	13.575	Cyclopentadienyl orbital
	−15.781	13.967	Cyclopentadienyl orbital
	−15.851	14.120	Cyclopentadienyl orbital
	−15.936	14.178	Cyclopentadienyl orbital
	−15.957	14.194	Cyclopentadienyl orbital
	−16.135	14.327	Cyclopentadienyl orbital
D′	−19.349	17.145	Cyclopentadienyl–Zr bond
	−19.665	17.447	Cyclopentadienyl–Zr bond

at 8.9 and 9.6 eV. The third (C) and fourth (D) bands range from 12 to 15 eV and from 16 to 19 eV, respectively. The origin of the low-intensity second band (B) centered about 11 eV raised several questions. The sensitivity of the intensity of this band to the experimental conditions suggested that it might be corresponding to other than $Cp_2Zr(BH_4)_2$ itself. It is of interest to note that this band appears both in the He(I) spectra of $Cp_2Zr(BH_4)_2$ and $Cp_2Hf(BH_4)_2$ [28]. Considering the fact that both compounds have been prepared by the same synthetic method, reducing the corresponding cyclopentadienyl halides by $LiBH_4$, the band in question might be related to the starting transition metal compound present as a contamination in the sample. It can also be due to thermal decomposition products formed at the temperature of the direct inlet probe (220°C). The latter idea has been partly confirmed when recording the photoelectron spectrum at various temperatures and investigating the intensity of this band. However, the high-level ab initio ionization energy calculations shed light on this problem. The calculated ionization energy (IE) of the title compound agree noticeably well with the experimental results showing that the band B (at least partly) originates from five orbitals of $Cp_2Zr(BH_4)_2$.

The He(II) photoelectron spectrum (Fig. 2) shows characteristic changes in relative band intensities. Main features include: (a) the substantial increase of the relative intensity of band A, and (b) the change in the shape of band B. This latter finding can be ascribed to the fact that the band intensities contributing to the shoulder of band B in the He(I) spectrum (ca. 12.8 eV) increase relative to the other components of this band. All these experimental facts together with the IE values make possible an approximate assignment of the PE spectrum: band A at the low-energy part of the spectrum originates from ionizations of high-energy Cp(π) and Cp–Zr orbitals with substantial d character; band B can be related to BH_4 ionizations; while bands C and D can be assigned to low lying Cp orbitals. This assignation is further confirmed by the ab initio molecular orbital calculations.

Table 4 summarizes the calculated molecular orbital energies together with the corresponding orbital characters. Because of the great number of closely spaced molecular orbitals it is meaningless to look for a precise correspondence between molecular orbitals and PE peaks. However, the structure of the PE spectrum—that is the grouping of molecular orbitals—is clearly reflected by the OVGF calculations. The orbitals can be divided into four groups as indicated in Table 4: the ionization energy from the first group of orbitals (A′) ranges from 8.519 to 9.735 eV; the second (B′) from 10.809 to 11.473 eV, while orbitals belonging to the third group (C′) correspond to an ionization energy of 12.353–14.327 eV. The fourth group consists of two orbitals with 17.145 and 17.447 eV ionization energies. Furthermore, the orbital characters can also be successfully related to the He(I)/He(II) relative intensity changes. According to the calculations the first group of orbitals are Cp(π) and Cp–Zr orbitals, the latter with substantial d-orbital contribution. The change in photoionization cross-sections of these orbitals with substantial d character is in agreement with the broadly demonstrated intensity changes published in connection with the photoelectron spectroscopy of transition metal systems [47].

4. Conclusions

The aim of these studies was to gain experimental and theoretical evidence for the bi- or tridentate ligation of the tetrahydrido groups attached to a bent sandwich fragment of Cp_2Zr. Both the calculated ab initio structure and the measured boron–zirconium distance give clear evidence of a bidentate ligation. The good agreement between the He(I)/He(II) photoelectron spectra and the calculated electronic structure of the complex lends further support to the reliability of the calculations.

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