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Covalent or not? Energy decomposition analysis of metal–metal bonding in alkaline-Earth dimetallocene complexes

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ABSTRACT

The geometries, metal–metal bond dissociation energies of Group 2 dimetallocene complexes $M_2(\eta^5\text{–}C_5H_5)_2$ (M = Be, Mg, Ca, Sr and Ba) have been calculated using density functional theory at the BP86 level with TZ2P basis sets. The nature of metal–metal bonding has been analyzed with an energy decomposition method. The results revealed that the M–M binding interactions in these nonpolar bonding alkaline-Earth metal complexes have more ionic character than covalent character, rather than the sole covalent bond. Molecular orbital calculations indicate that, for the heavier alkaline-Earth metal (Ca, Sr and Ba) compounds, substantial $(n-1)d$ character is found in the δ bonding between metal and cyclopentadiene (Cp) ring, while there is few δ bonding interaction between M–M bond due to longer M–M bond distance.

1. Introduction

During the last two decades the metallocenes chemistry of the main-group elements has experienced remarkable development. A large number of main-group metallocenes compounds with elements of the Groups 1, 2, 13, 14 and 15, have been synthesized and structurally characterized and the main principles of structure, bonding and reactivity are well understood [1–4]. Otherwise, following the report on the synthesis and structure of an unprecedented dimetal core cyclopentadienyl (Cp) compound $[Zn_2(\eta^5\text{–}C_5Me_5)_2]$ [5], dimetallocene has arisen more attentions quickly. The unique nature of this compound has motivated an astonishingly large number of both experimental and theoretical investigations [6–16]. The alkaline-Earth metal metallocenes are an especially attractive family of metallocenes [17,18]. Carmona et al. review recent developments in the chemistry of beryllocenes [19]. The energy decomposition analysis (EDA) of the interactions suggests that the bonding between metal and cyclopentadienyl ligand in the alkaline-Earth metallocenes is mainly caused by electrostatic forces [20]. For the dimetallocene, a theoretical study of the analogous model compounds $[M_2(C_5H_5)_2]$ (M = Be, Mg, Ca) has been reported by Xie et al. [21]. Just recently, Merino et al. theoretically predicted geometries and stabilities of the multimetallocenes CpM_nCp compounds and investigated the metal–Cp interactions using EDA method [22]. Moreover, Green et al. reported some novel thermally stable Mg(I) compounds and revealed that central Mg^{2+} units that have single covalent Mg–Mg bonding interactions [23]. We have analyzed the bonding in Group 12 transition metallocenes, the EDA result indicates metal–metal bonds have slightly more attractive contributions from classical electrostatic interactions than the attractive orbital interactions [24]. In this letter we present results for the alkaline-Earth metals (+1 oxidation state) metallocenes $[M_2(Cp)_2]$ (M = Be–Ba,) by EDA and electron localization function (ELF). Detailed theoretical calculations aimed to shed some light on the nature of the metal–metal bonding in these systems.

2. Theoretical methods

Energies and geometries were calculated using the generalized gradient approximation (GGA) of DFT at the BP86 level. GGA proceeds from the local density approximation (LDA) where exchange is described by Slater's Xα potential and correlation is treated in the Vosko–Wilk–Nusair (VWN) parametrization. Scalar relativistic effects have been considered using the zero-order regular approximation (ZORA) [25]. The basis sets used are of triple-ζ quality augmented by two sets of polarization functions (TZ2P), and a frozen-core approximation was not used. To assure the usage of ground-state geometries in all calculations, the Hessian matrix was checked for the absence of imaginary entries.

The bonding interactions between the two equal metal fragments have been analyzed by means of the energy decomposition analysis implemented in ADF package, which is based on the EDA method of Morokuma and the extended transition state (ETS) partitioning scheme developed by Ziegler and Rauk. The overall bond

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energy ΔE can be determined from interaction energy (ΔE_{int}) and the fragment preparation energy ΔE_{prep}, the instantaneous ΔE_{int} between the two fragments can be divided into three main components [Eq. (1)], details about EDA can be found in the literature [26].

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}} \tag{1}$$

The bonding properties of the dimetallocene have also been studied according to topological analysis of the ELF [27], which is a robust descriptor of chemical bonding based on topological analyses of local quantum mechanical functions related to the Pauli exclusion principle.

All calculations were performed using the Amsterdam Density Functional (ADF 2006.01) program [26]. The topological analysis of ELF has been performed using the DGrid programs[28].

3. Results and discussion

3.1. Geometric structures

The calculation of the vibrational frequencies revealed that all structures are minima on the potential energy surface (PES), which has D_{5h} symmetry. Table 1 gives the calculated most important structural parameters of the investigated metallocenes. Apparently, the M–M and M–C bond distance in the D_{5h} symmetric $C_5H_5M–MC_5H_5$ increase descending the periodic table from Be to Ba. However, the C–C bond distance in Cp ligand does not change much and amounts to ca. 1.42 Å throughout the series. This agrees satisfactorily with previous theoretical work [21,22], which also yield a monotonic increase of the M–M and C–M bond along $Be_2(Cp)_2$, $Mg_2(Cp)_2$ and $Ca_2(Cp)_2$, while the M–M value presented here is somewhat larger than the previous result by 0.004–0.089 Å. The calculated bond parameters which are given here should be more reliable, because, the calculated structure is in agreement with discussion of the experimental structure for $Be(Cp)_2$ at similar BP86/TZP level [20] and the higher quality of the basis sets used in this work. Furthermore, in our recent work, the calculated Zn–Zn distance (2.306 Å) is in excellent agreement with the experimental values (2.305 Å) for $Zn_2(\eta^5–C_5Me_5)_2$ use the same method [24]. It should be noted, for Ca compound, Merino et al. [22] obtain Ca–Ca of 3.961 Å with same level, but the result is different from the present ones of 3.823 Å. Calculation of the vibrational frequencies at the Ca–Ca of 3.961 Å geometry shows that it is not minima on the potential energy surface with an imaginary frequency of $-11.6\ \mathrm{cm}^{-1}$. Moreover, Westerhausen et al. give a BP86/TZVPP Ca–Ca of 3.806 Å [29], rather close to the result of this work.

To the best of our knowledge, the complexes with M = Sr and Ba have not been calculated by *ab initio* or DFT methods before. Thus, the data in Table 1 are the first complete set of theoretically predicted geometries of Group 2 transition dimetallocenes. The comparison of the alkaline-Earth dimetallocene $M_2(Cp)_2$ with the metallocene species $Be(Cp)_2$ –$Ba(Cp)_2$ shows same trend of metal and Cp ligand geometrical parameters. With the increase of atom radii, the M–M and M–C bond elongate substantially by 0.3–0.7 Å and 0.1–0.4 Å from Be to Ba, respectively. These M–M distances are much shorter than the experimental value for the weakly bound diatomic M_2 (M–M = 2.45, 3.597, 4.707 Å along Be, Mg and Ca) [21], indicating the cyclopentadienyl groups strengthen the M–M bonding than that for the metal dimer. This reveals there are comparable M–M bonding interactions in all of these dimetallocene compounds. In order to investigate the nature of M–M bonding in these metallocenes, in the following section we will do this in a quantitative way by using the results of molecular orbital and the energy decomposition analysis [26].

3.2. Fragment orbital (FO) and ELF analysis

The bonding situation in alkaline-Earth monometallocenes $M(Cp)_2$ (M = Be–Ba) compounds has been analyzed with qualitative bonding models [2,4]. Recent calculation analysis showed that the bonding of the Cp ligand to the alkaline-Earth elements is considered to be predominantly ionic [20,30]. In this work, we focus on nature of the metal–metal bonding derives from FO calculation of the orbital interaction in all alkaline-Earth dimetallocenes $M_2(Cp)_2$. Fig. 1 shows a qualitative orbital correlation diagram for the formation of MOs in $Be_2(\eta^5–C_5H_5)_2$ using the fragment $Be(\eta^5–C_5H_5)$.

The results of Kohn–Sham MO analysis indicate that the Be–Be bonding interaction mainly resides in the HOMO, and same results can be found in Mg compound. The bonding interaction mainly comes from the $<ns|ns>$ bond overlap between two ns singly occupied molecular orbitals (SOMO) in M_2Cp_2 (see Fig. 1). The fragment orbital calculations reveal that it has a contribution of $6a_1$ orbitals in fragment $Be(\eta^5–C_5H_5)$ close to 97%, the metal–metal bond involves mostly the Be 2s orbitals (more than 78%) and $2p_z$ orbitals of 22%. In Mg complex, the bonding HOMO comes from combination of two $8a_1$ fragment orbital which is about 98%, there are still two principal bonding components: 82% 3s orbitals and 17% $3p_z$ orbitals from Mg. This is comparable with that calculated for the novelly stable MgMg bond compound, $\{Mg[(Ar'N)_2C(NMe_2)]\}_2$ (Ar′ is $C_6H_3Me_2$-2,6) (93.2% s-, 6.0% p-character), which has a different ligands [23]. Note that the relative contribution in the remaining heavier alkaline-Earth complexes shows the different

Table 1
BP/TZ2P calculated values of the optimized geometrical parameters of investigated compounds (bond length R in angstrom, bond angle θ in degree).

	Method	R(M–M)	R(M–C)	R(C–C)	θ(M–M–C)	Ref.
CpBeBeCp	BP86/TZ2P	2.081	1.979	1.422	142.2	This work
	BP86/TZ2P	2.077	1.966	1.421	142.1	[22]
	B3LYP/DZP	2.057	1.968	1.425		[21]
	BP86/DZP	2.066	1.972	1.434		[21]
CpMgMgCp	BP86/TZ2P	2.790	2.378	1.422	149.4	This work
	BP86/TZ2P	2.809	2.376	1.424	149.4	[22]
	B3LYP/DZP	2.766	2.376	1.428		[21]
	BP86/DZP	2.786	2.378	1.436		[21]
CpCaCaCp	BP86/TZ2P	3.823	2.659	1.422	153.0	This work
	BP86/TZ2P	3.961	2.661	1.421	153.0	[22]
	B3LYP/DZP	3.740	2.668	1.425		[21]
	BP86/DZP	3.734	2.655	1.433		[21]
CpSrSrCp	BP86/TZ2P	4.171	2.805	1.420	154.5	This work
CpBaBaCp	BP86/TZ2P	4.662	2.953	1.430	155.9	This work