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A DFT Study on Dinuclear Metallocenes RMMR [R= $(BCO)_5$, $(BNN)_5$; M = Be, Mg, Ca, Zn, Cd]

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A series of dinuclear metallocenes with formula RMMR [R= $(BCO)_5$, $(BNN)_5$; M = Be, Mg, Ca, Zn, Cd] are investigated via density functional theory. All these compounds contain two M[η^5-$(BCO)_5$] fragments or two M[η^5-$(BNN)_5$] fragments with a direct metal−metal single σ bond. Detailed NBO analyses show that the metal−ligand interactions are predominantly ionic in nature and each metal atom is in its +1 oxidation state. NBO analyses indicate that the interaction between the B−B bonds and metal−metal antibond has played a role in the stabilities of these compounds.

1. Introduction

Recently, decamethyldizincocene, Cp*ZnZnCp* (Cp* = C_5Me_5), containing two eclipsed Cp*Zn fragments where the homonuclear metal Zn−Zn bond is collinear with the C_5 symmetry axes of the Cp* rings, has been unexpectedly synthesized and successfully isolated by Resa et al.[1] This encouraging discovery opened a new dimension to metallocene chemistry and motivated further studies on dinuclear metallocenes involving transition metal and main-group metal.[2−17] Experimentally, Wang et al. reported the second synthesized compound with a Zn−Zn bond, R*ZnZnR* (R*= [{(2,6-$Pr^i_2C_6H_3$)N(Me)C}$_2$CH]).[13] Wu and Stace prepared and studied the fragmentation patterns of $M_2L_n^+$ (M = Zn, Cd; L= pyrrole, furan; $n = 1−5$) by combination of a pick-up technique and high-resolution mass spectrometry.[17] Theoretically, Xie et al. predicted a series of relatively stable species containing main-group elements, CpMMCp (Cp = C_5H_5; M = Be, Mg, Ca), and concluded that the structural pattern discovered for zinc is more generally applicable.[4] Xie et al. also computationally investigated a second type of energetically preferred binuclear metallocenes CpCuCuCp and CpNiNiCp, in which the metal−metal bond axis is perpendicular to rather than collinear with the C_5 symmetry axes of the Cp rings.[5] Kang theoretically studied various complexes of extended Cp ligands with Zn and Cd atoms of +1 oxidation state.[6] Timoshkin and Schaefer reported a series of novel main-group bis-element metallocenes formed by donor−acceptor interactions of CpM and M′Cp (M = Li, Na, K; M′ = B, Al, Ga) using B3LYP density functional method and predicted the species containing boron, which are stabilized by electrostatic interactions, are the most stable and viable synthetic targets.[11] Further, to explore whether the bis-element sandwich with acyclic ligands exists, Merino et al. investigated a series of structures with the general formula CpM−M*Pyl (M = B, Al, Ga; M* = Li, Na; Pyl = C_5H_7) by means of density functional theory, which are the first examples of donor−acceptor heteroleptic open sandwiches.[16] Thus, on the other hand, a question is raised naturally: Do other five-membered ring ligands exist which can stabilize the M_2^{2+} unit, in addition to Cp and Cp*? To our knowledge, there are no such reports yet. $(BCO)_5^-$ anion was predicted stable by Schleyer et al.[18] as a new five-membered ring ligand. $(BNN)_5^-$ is isoelectronic with $(BCO)_5^-$ anion. In the present work, hence, the title compounds RMMR [R= $(BCO)_5$, $(BNN)_5$; M = Be, Mg, Ca, Zn, Cd] are surveyed to explore their structures, stabilities, bonding mechanisms, and the influence of these two five-membered ring ligands on the stability of M_2^{2+} unit via density functional theory (DFT).

2. Theoretical Methods

Two DFT methods are employed in the present study. One is the hybrid Hartree−Fock (HF)/DFT method known as B3LYP which combines Becke's three-parameter functional[19] with the Lee−Yang−Parr correlation functional.[20] The other one is the pure DFT method known as the BP86 which incorporates Becke's 1988 exchange functional[21] with Perdew's 1986 correlation functional.[22] Using B3LYP and BP86 methods with SDD pseudo potential and basis set for Cd atom and 6-311G** basis set for other atoms, the geometries of all structures are fully optimized, and the harmonic vibrational frequencies are determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The number of imaginary vibrational frequencies (N_{imag}) determines if the optimized structures are local minima or higher-order saddle points. The zero-point energy (ZPE) of each species is used to correct its total energy. The NBO[23] analyses are performed at the same levels of theory, to understand the bonding character of these compounds. All of the computations were carried out with the Gaussian 03 program,[24] exercising the specific grid (140 radial shells, 974 angular points) for evaluating integrals numerically, while the tight designations are the defaults for the self-consistent field and geometry optimization convergences. In the present case, the B3LYP and BP86 methods agree with each other fairly well for predicting the structural and electronic characteristics of all molecules. Thus, the results from B3LYP method are mainly discussed in the text.

3. Results and Discussion

3.1. Electronic and Geometric Structures. Similar to CpBeBeCp, both the $(BCO)_5BeBe(BCO)_5$ (**1a**) and $(BNN)_5$BeBe-

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TABLE 1: Zero-Point Energies (ZPE, kcal/mol), Total Energies after ZPE Correction (E_{ZPE}, Hartrees), and the Number of Imaginary Vibration Frequency (N_{imag}); WBI of M−B and M−M Bonds; NAC on Each B and the Metal Atoms (q_B and q_M); and s Character (% s) and e_{occ} of M−M Bonds for All the Dinuclear Compounds

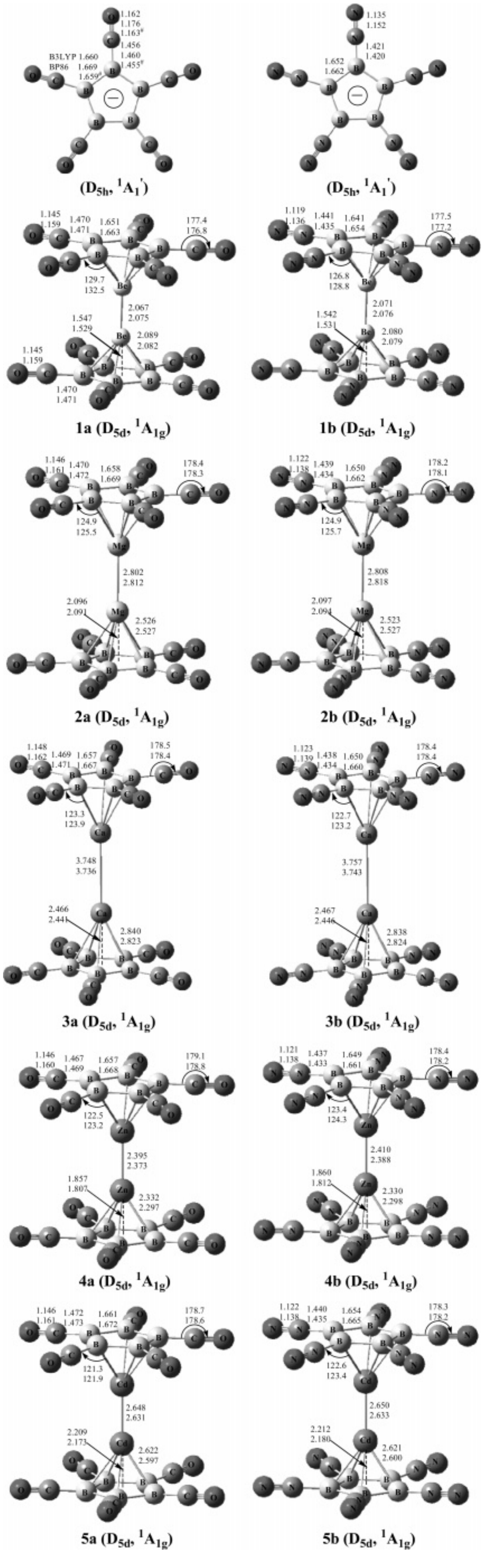
				M−B			M−M		
	ZPE	E_{ZPE}	N_{imag}	WBI	q_B	q_M	WBI	% s	e_{occ}
				B3LYP					
1a	83.6	−1411.56356	0	0.044	−0.473	0.890	0.865	92.6	1.938
1b	84.2	−1373.26972	0	0.050	−0.241	0.866	0.853	92.7	1.937
2a	81.3	−1782.29314	0	0.024	−0.451	0.933	0.856	97.0	1.955
2b	81.7	−1743.99073	0	0.029	−0.218	0.911	0.837	97.0	1.954
3a	80.5	−2737.30334	1[a]	0.030	−0.435	0.933	0.893	95.2	1.954
3b	80.9	−2698.99742	0	0.034	−0.204	0.914	0.880	95.6	1.947
4a	81.2	−4940.69247	0	0.043	−0.461	0.967	0.753	98.7	1.941
4b	81.6	−4902.38414	0	0.048	−0.230	0.946	0.719	98.7	1.939
5a	80.1	−1717.63787	0	0.046	−0.428	0.843	0.758	97.7	1.972
5b	80.4	−1679.33789	0	0.052	−0.194	0.808	0.729	97.6	1.971
				BP86					
1a	80.9	−1411.58753	0	0.048	−0.448	0.900	0.824	93.3	1.902
1b	81.5	−1373.35024	0	0.053	−0.210	0.875	0.814	93.3	1.903
2a	78.7	−1782.32694	1[a]	0.026	−0.426	0.932	0.842	97.4	1.947
2b	79.2	−1744.08280	0	0.032	−0.187	0.908	0.818	97.3	1.943
3a	77.3	−2737.44920	1[b]	0.034	−0.410	0.925	0.883	95.4	1.945
3b	78.3	−2699.20176	0	0.039	−0.173	0.908	0.861	95.6	1.938
4a	78.7	−4941.16805	0	0.052	−0.440	0.980	0.730	98.5	1.934
4b	79.2	−4902.91674	0	0.057	−0.203	0.956	0.691	98.5	1.931
5a	77.6	−1717.79179	0	0.050	−0.403	0.839	0.731	97.9	1.967
5b	78.0	−1679.55038	0	0.056	−0.162	0.804	0.698	97.8	1.964

[a] An imaginary vibration frequency of 0.1i. [b] An imaginary vibration frequency of 0.7i.

$(BNN)_5$ (**1b**) are energetic minima. The energy differences between D_{5d} and D_{5h} conformations of **1a** and **1b** are less than 0.1 kcal/mol, indicating a very flat potential energy surface (PES) with respect to the internal rotation. The geometry parameters of D_{5h} conformations of **1a** and **1b** are almost identical to those of D_{5d} conformations. The same is true for $(BCO)_5MgMg(BCO)_5$ (**2a**) and $(BNN)_5MgMg(BNN)_5$ (**2b**). The geometries of D_{5d} and D_{5h} isomers of $(BCO)_5CaCa(BCO)_5$ (**3a**) are also very close to each other, and there is only an energy difference within 0.001 kcal/mol between these two isomers, as well as $(BNN)_5CaCa(BNN)_5$ (**3b**). As listed in Table 1, $(BCO)_5CaCa(BCO)_5$ (**3a**) with D_{5d} symmetry is calculated to have a very small imaginary vibration frequency (0.1i) related to internal rotation around the Ca−Ca bond axis, while the D_{5h} conformation is calculated to be a genuine minimum with all real vibration frequencies and whose corresponding vibration frequency is 0.7 cm^{-1}. Such a small imaginary vibration frequency of 0.1i might result from the particular flatness of the PES and the limitation in the numerical integration procedures used in the DFT computations, and it is so small that it can be neglected. Thus, **3a** with D_{5d} symmetry is an energetic minimum identical or very close to the structure of the energetic minimum in question. In fact, the distance between the centers of two ligands in **3a** is sufficiently long (8.680 Å) for the two ligands to rotate freely around the Ca−Ca bond axis, considering the flatness of its PES and the electrostatic character of the Ca−ligand bonding in **3a** (positive charge of nearly +1 resides on each Ca atom). Similar computations performed to the transition metals Zn and Cd analogies also show that $(BCO)_5ZnZn(BCO)_5$ (**4a**), $(BNN)_5ZnZn(BNN)_5$ (**4b**), $(BCO)_5CdCd(BCO)_5$ (**5a**), and $(BNN)_5CdCd(BNN)_5$ (**5b**) with D_{5d} symmetry are genuine minima with all real vibration frequencies, showing geometries and energies similar to those of their corresponding isomers with D_{5h} symmetry. Hence, we only show the energies and geometries of D_{5d} conformations for these dinuclear compounds in Table 1 and Figure 1, respectively.

The M−M distances of the title compounds and individual M_2^{2+} units are tabulated in Table 2, as well as the M−M stretching vibration frequency. As we can see, the M−M distances are predicted to be 2.067 Å for **1a** (2.071 Å for **1b**), 2.802 Å for **2a** (2.808 Å for **2b**), and 3.748 Å for **3a** (3.757 Å for **3b**), comparable to the corresponding M−M distances for CpMMCp calculated at the B3LYP/DZP level of theory,[4] which suggests the effect of ligands $(BCO)_5$ and $(BNN)_5$ on the M_2^{2+} units is similar to that of the ligand Cp. The calculated Zn−Zn distances of **4a** and **4b** are 2.395 Å and 2.410 Å, respectively, and the Cd−Cd distances of **5a** and **5b** are 2.648 Å and 2.650 Å, in line with the experimental values 2.305 Å or 2.359 Å and theoretical value 2.336 Å of the Zn−Zn single bond[1,5,13] and experimental value 2.58 Å of the Cd−Cd single bond.[25,26] In fact, compared to the individual M_2^{2+}, the M−M bonds of title compounds are shortened by about 3∼5%, except that the Ca−Ca bonds of **3a** and **3b** show almost the same distance to the individual Ca_2^{2+}, and the M−M stretching vibration of these dinuclear compounds shows considerable blue shift. Obviously, both of these exhibit the stabilization effect of ligands $(BCO)_5$ and $(BNN)_5$ on the M_2^{2+} units. According to NBO analyses, the Wiberg bond indices (WBI) of M−M bonds are near 1, and the electron occupancies (e_{occ}) of the M−M bonding orbitals are close to 2. The M−M bonds have dominant (>90%) s character, and the natural atom charge (NAC) on each metal atom approaches +1. That indicates there exist single M−M σ bonds in these dinuclear compounds, and each metal atom is in its +1 oxidation state. It is noted that the NAC on each B atom of $(BCO)_5MM(BCO)_5$ is almost twice that on each B atom of $(BNN)_5MM(BNN)_5$, which might be caused by the difference of electronegativity between the N and C atoms that are adjacent to B atoms.

The WBI of M−B bonds are predicted to be less than 0.1. Thus, the bonding between the metal atoms and the ligands is predominantly ionic in nature and the electrostatic interaction dominates the metal−ligand interaction, with one electron of the metal atom transferred to the connected B_5 ring of the ligand.



(D_{5h}, ${}^1A_1'$) (D_{5h}, ${}^1A_1'$)

1a (D_{5d}, ${}^1A_{1g}$) **1b** (D_{5d}, ${}^1A_{1g}$)

2a (D_{5d}, ${}^1A_{1g}$) **2b** (D_{5d}, ${}^1A_{1g}$)

3a (D_{5d}, ${}^1A_{1g}$) **3b** (D_{5d}, ${}^1A_{1g}$)

4a (D_{5d}, ${}^1A_{1g}$) **4b** (D_{5d}, ${}^1A_{1g}$)

5a (D_{5d}, ${}^1A_{1g}$) **5b** (D_{5d}, ${}^1A_{1g}$)

Figure 1. Optimized structures for compounds $(BCO)_5^-$, $(BNN)_5^-$, and RMMR [R = $(BCO)_5$, $(BNN)_5$; M = Be, Mg, Ca, Zn, Cd]. Bond lengths are in angstroms, and angles are in degrees. #From ref 18.

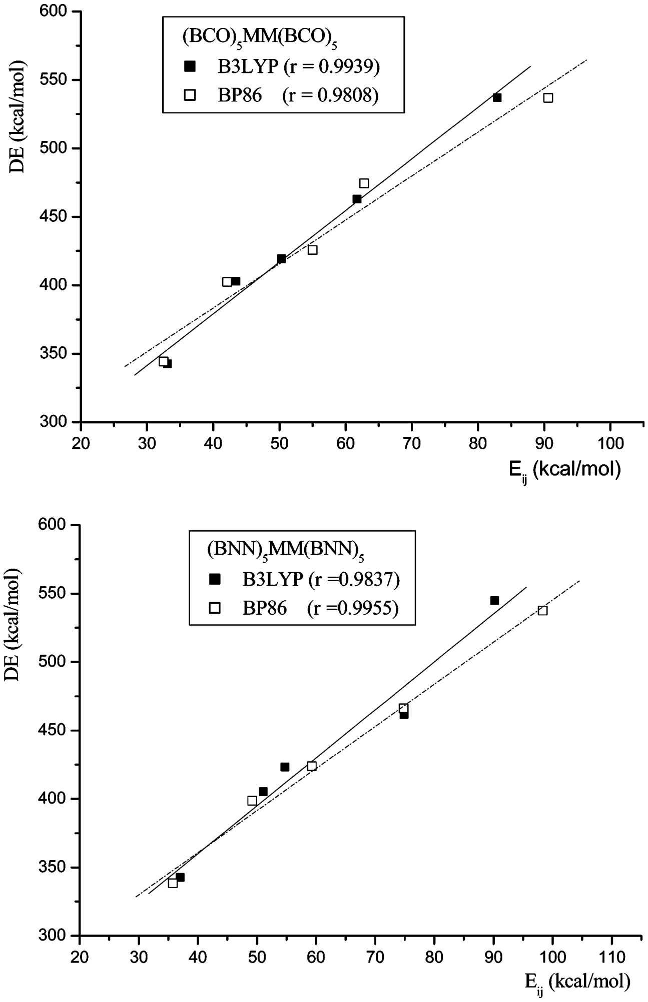


Figure 2. Correlation of the DE versus the E_{ij} of the dinuclear compounds.

Consequently, this electron and the other five electrons of B_5 p orbitals form a conjugated Π_5^6, and the ligands $(BCO)_5$ in $(BCO)_5MM(BCO)_5$ and $(BNN)_5$ in $(BNN)_5MM(BNN)_5$ are close to the geometries of individual $(BCO)_5^-$ and $(BNN)_5^-$ anions, with the NN or CO unit slightly out of the plane. The NBO analyses show that the interaction of the B−B bonds with the M−M antibond significantly stabilizes the compounds. The interaction energy comes from the second-order perturbative estimates of donor−acceptor (bond−antibond) interactions in the NBO basis. These donor−acceptor interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals, and thus for each donor NBO (i) and acceptor NBO (j), the stabilization energy is defined as

$$E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i}$$

where q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements (orbital energies) of the Fock matrix, and $F(i,j)$ is the off-diagonal NBO Fock matrix element.[27] The interaction energy E_{ij} of the B−B bonds with the Be−Be antibond is totally 74.9 kcal/mol for **1b**, 13.2 kcal/mol more than that for **1a** (see Table 2). It means these two ligands have played an important role in the stabilities of **1a** and **1b**, with the ligand $(BNN)_5$ more significant than $(BCO)_5$. The E_{ij} values for Mg analogies are 43.4 kcal/mol (**2a**) and 51.1 kcal/mol (**2b**), which shows the

TABLE 2: Bond Distance and Stretching Vibration Frequency of Metal−Metal Bonds (b_{M-M} and ν_{M-M}); Dissociation Reaction Energies (DE, in kcal/mol) and Interaction Energies (E_{ij}, in kcal/mol) of the B−B Bonds with the Metal−Metal Antibond of Herein Reported Dinuclear Compounds

	B3LYP				BP86			
	b_{M-M}	ν_{M-M}	DE	E_{ij}	b_{M-M}	ν_{M-M}	DE	E_{ij}
Be_2^{2+}	2.137	623.7			2.149	610.1		
$(BCO)_5BeBe(BCO)_5$	2.067	783.8	463.0	61.7	2.075	767.4	474.4	62.8
$(BNN)_5BeBe(BNN)_5$	2.071	784.2	461.6	74.9	2.076	768.8	466.2	74.8
Mg_2^{2+}	2.928	235.4			2.950	227.6		
$(BCO)_5MgMg(BCO)_5$	2.802	391.8	403.0	43.4	2.812	386.8	402.4	42.1
$(BNN)_5MgMg(BNN)_5$	2.808	388.8	405.3	51.1	2.818	382.1	398.6	49.2
Ca_2^{2+}	3.748	143.0			3.719	147.7		
$(BCO)_5CaCa(BCO)_5$	3.748	266.8	342.6	33.1	3.736	266.0	344.3	32.5
$(BNN)_5CaCa(BNN)_5$	3.757	269.7	342.7	37.0	3.743	266.3	338.5	35.8
Zn_2^{2+}	2.542	153.4			2.527	150.6		
$(BCO)_5ZnZn(BCO)_5$	2.395	313.1	537.1	82.9	2.373	313.8	536.9	90.6
$(BNN)_5ZnZn(BNN)_5$	2.410	311.6	544.8	90.2	2.388	311.6	537.5	98.3
Cd_2^{2+}	2.798	130.8			2.789	127.9		
$(BCO)_5CdCd(BCO)_5$	2.648	243.1	419.4	50.3	2.631	244.4	425.8	55.0
$(BNN)_5CdCd(BNN)_5$	2.650	245.5	423.2	54.7	2.633	244.5	423.8	59.3

interaction between the B−B bonds and the M−M antibond for Mg analogies is slightly smaller than that for Be analogies. The interaction energy E_{ij} for Ca analogies are least among compounds herein reported, only 33.1 kcal/mol for **3a** and 37.0 kcal/mol for **3b**, respectively, which is in accord with the least change of the Ca−Ca bond distance (compared to the change of M−M bond distance of other herein reported dinuclear compounds). The E_{ij} values of the interaction between the B−B bonds and the Zn−Zn antibond are larger than other herein reported compounds, up to 82.9 kcal/mol for **4a** and 90.2 kcal/mol for **4b**, which indicates that the ligands have significantly stabilized **4a** and **4b**. The corresponding E_{ij} of **5a** and **5b** are 50.3 and 54.7 kcal/mol.

3.2. Stabilities of Compounds. The stabilities of these dinuclear compounds have been estimated by the following reaction (based on the energies after ZPE correction):

$$\mathrm{RMMR} \rightarrow 2\mathrm{R}^- + \mathrm{M}_2^{\ 2+}$$
$$[\mathrm{R} = (\mathrm{BCO})_5, (\mathrm{BNN})_5; \mathrm{M} = \mathrm{Be, Mg, Ca, Zn, Cd}]$$

All the compounds R^- with D_{5h} symmetry and M_2^{2+} with $D_{\infty h}$ symmetry are predicted to be genuine minima. The dissociation reaction energies (DE) are tabulated in Table 2. This reaction mainly refers to the break of M−B bonds between the M_2^{2+} and the ligands R. Therefore, the DE might show the stabilities of these compounds with respect to the dissociation and be related to the stabilization of the ligands $(BCO)_5$ and $(BNN)_5$ on the M_2^{2+} units. As we can see, the reaction is considerably endothermic for all the dinuclear compounds since their DE are fairly large positive values, which suggests that they are very stable with respect to the dissociation reaction and the interaction between metal atoms and the ligands is fairly strong. It is noted that the stabilities of these dinuclear compounds RMMR [R = $(BCO)_5$, $(BNN)_5$; M = Be, Mg, Ca, Zn, Cd] are consistent with the order of the E_{ij} values. Compounds **4a** and **4b** are the most stable with the largest E_{ij} values, while **3a** and **3b** are the least stable with the least E_{ij} values. A linear correlation ($r > 0.98$) is obtained by plotting the DE values against the E_{ij} values (see Figure 2), indicating that the interaction of the B−B bonds with the M−M antibond is one of the important factors in the stabilities of these dinuclear compounds.

4. Summary

In this paper, a series of compounds with general formula RMMR [R = $(BCO)_5$, $(BNN)_5$; M = Be, Mg, Ca, Zn, Cd] are investigated using DFT methods. All these compounds contain two M[η^5-$(BCO)_5$] fragments or two M[η^5-$(BNN)_5$] fragments with a direct metal−metal bonding. Detailed NBO analyses indicate that the metal−metal bonds of these compounds are single covalent σ bonds, with each metal in its +1 oxidation state, and the metal−ligand bonding is essentially ionic. The single metal−metal bonds are composed of s orbitals primarily. The metal−metal distances are shortened due to the coordination of ligands $(BCO)_5$ and $(BNN)_5$ in the title compounds, similar to the effect of ligand Cp on the M_2^{2+} units in the corresponding CpMMCp compounds, and the metal−metal stretching vibrations shows considerable blue shift. All the dinuclear compounds RMMR [R = $(BCO)_5$, $(BNN)_5$; M = Be, Mg, Ca, Zn, Cd] are very stable with respect to the dissociation to $M_2^{2+} + 2R^-$. A linear correlation ($r > 0.98$) is obtained between the dissociation energy DE and the interaction energy E_{ij} of the B−B bonds with the metal−metal antibond, indicating that the interaction of the B−B bonds with the M−M antibond is one of the important factors in the stabilities of these dinuclear compounds.

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