

## **Supporting Information**

### **Steric and Electrostatic Effects in Compounds with Centered Clusters**

#### **Quantified by Bond Order Analysis**

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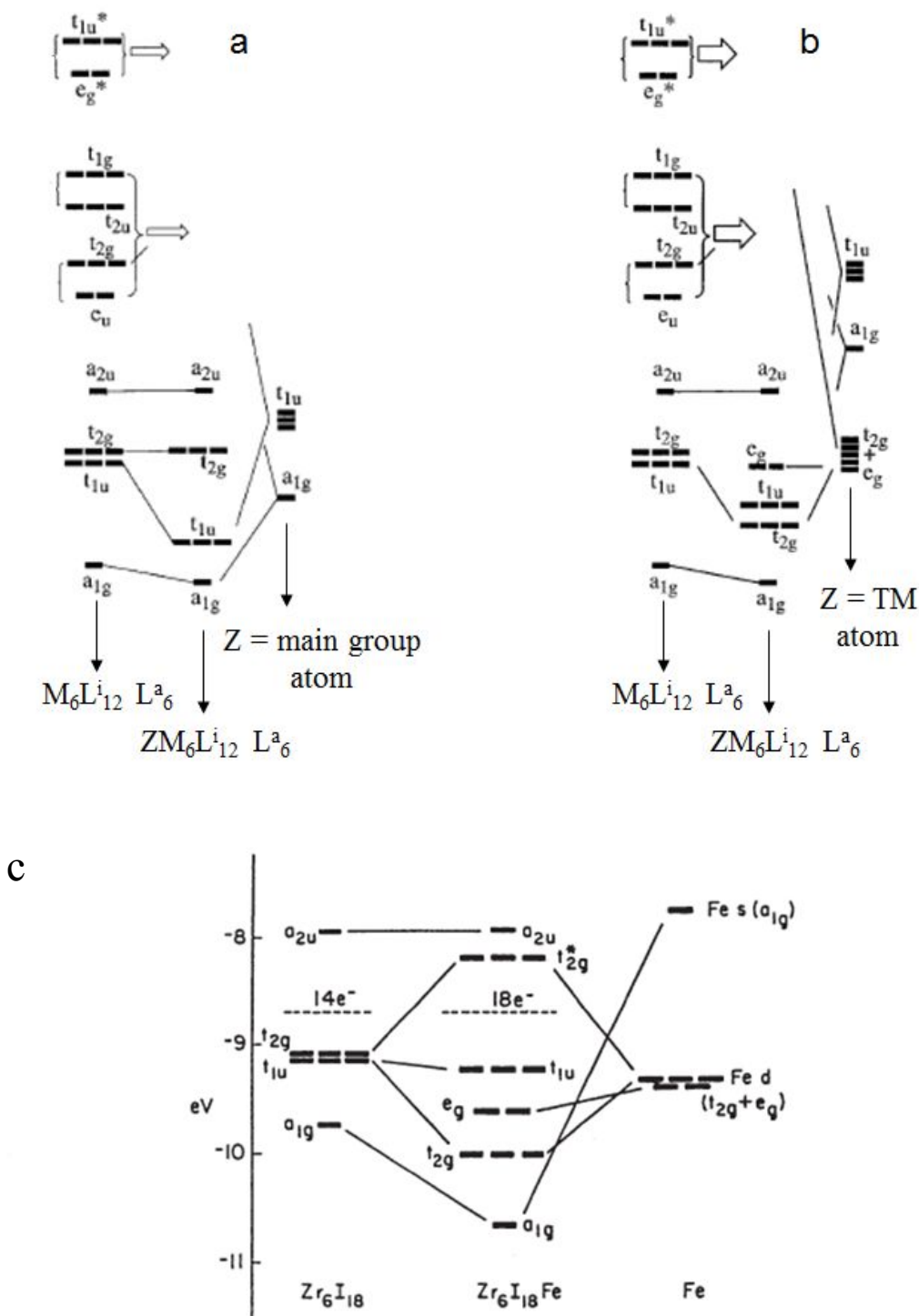
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**Figure S1.** Molecular Orbital diagrams for the octahedral  $M_6$ -clusters with interstitial  $Z$  atom: a -  $Z$  is a main group element, b and c -  $Z$  is the TM atom. Note the difference in the position of the non-bonding orbitals  $e_g$ . Diagrams a and b are proposed in ref.<sup>1</sup>, while diagram c is taken from ref.<sup>2</sup>

### **On the application of the Bond Valence Model (BVM) in material research:**

- The BVM is systematically applied in crystal chemistry to check the reliability of structure solutions (The Model is, in fact, a vital part of crystallographic programs), and to determine the cation oxidation states,<sup>3</sup> in particular, in coordination compounds.<sup>4</sup>
- A unique BVM ability to calculate the bond strains from the experimental interatomic distances and relate them to material stability was used for crystal structure predictions, in particular, for perovskites.<sup>5</sup> We used the BVM to quantify the bond strains in cathodes for Li and Na batteries, and showed that this method can predict and explain the material stability even better than traditional calculations of formation energy.<sup>6</sup> We also used the model to describe the lattice strains in Chevrel Phases, well-known superconductors, ionic conductors and unique cathodes for Mg batteries.<sup>7</sup>
- The BVM was successfully used for modeling of ionic transport in solids, in particular, in cathode materials for Li batteries.<sup>8</sup> We used the BVM to explain the unusual mobility of multivalent cations in Chevrel phases.<sup>9</sup>
- The BVM was also used for accurate molecular dynamics simulations.<sup>10</sup>

The importance of the BVM application is evident from the high citation numbers for the publications mentioned above, e.g., 1252, 627, 597 and 389 for refs. 5a, 3, 5b and 4, respectively. However, almost all the studies are related to compounds without metal-metal bonds, while for the latter the BVM is not used. It seems important to understand the reason of this phenomenon.

As it is clear from the main text, the BVM is based on the exponential correlation between the bond length and respective *effective* Bond Order (BO). Due to relatively low bond strains, which may arise in the compounds without metal-metal bonds, the effective BOs in the latter are close to the formal ones (see the main text). In contrast, in compounds with metal-metal bonds, due to the matrix effect, the difference between effective and formal BOs for the same M-M bond may reach 1 v.u. As a result, when the founder of cluster chemistry, F. A. Cotton, used the *formal* BOs in his study, he did not find any clear correlation between the latter and the respective M-M bond length.<sup>11</sup> It seems that this negative result obtained by Cotton provoked the long-time neglect of the BVM in cluster chemistry. Indeed, in his book Cotton wrote:<sup>12</sup> “It is a general qualitative rule in chemistry that bond lengths and bond orders are inversely related...

However, there is no a priori reason to expect that similar procedures will (or will not!) work in the very different realm of metal-to-metal bonds. Experience is the only test, and experience thus far has shown that M–M bonds cannot usefully be treated in such a way...We condemn as foolish and hopeless any effort to associate a unique, quantitative bond order with each and every metal-metal internuclear distance.”

Nevertheless, our recent works<sup>13</sup> unambiguously showed the validity of two basic principles proposed by Pauling, namely, i) the exponential correlation between bond lengths of the metal-metal bonds and their *effective* BOs, and ii) BO conservation principle for the M atoms; thus confirming the applicability of the BVM for cluster compounds. Based on the logical and interesting results obtained in our studies, we believe that the traditionally negative opinion of cluster chemists about the BVM is a serious problem, because it deprives them of a very simple and useful method of bonding description.

**Three methods used in this work for the BV parameters determination.** The empirical BV parameters are well known for the cation-anion pairs,<sup>14</sup> but their determination for the metal-metal bonds is not trivial.<sup>13b</sup> In this work three different ways to determine the empirical BV parameters were used. The first one is a universal method proposed by O'Keeffe & Brese in 1991.<sup>15</sup> The  $b_{ij}$  parameter was assumed to be constant and equal to 0.37 Å, while  $R_{0\ ij}$  was calculated by the following equation:

$$R_{0\ ij} = r_i + r_j - \{r_i r_j (\sqrt{c_i} - \sqrt{c_j})^2\} / (c_i r_i + c_j r_j), \quad (S1)$$

where  $r$  and  $c$  values are constant for a given chemical element; they are related to its size and electronegativity, respectively. The universal method, widely used in crystal chemistry for the cation-anion pairs,<sup>3, 6, 14a</sup> seems to be very attractive for the description of the M-M and M-Z bonding in the  $ZM_6$ -clusters, because, in general, Eq S1 allows for the  $R_{0\ ij}$  calculation for any atom pair, including metal-metal interactions. However, as far as we know, the BV parameters of the metal-metal pairs predicted by this method were never verified in practice. Thus, an essential part of our study was devoted to the applicability of these parameters to the M-M and M-Z bonds.

The second adopted method is the one proposed in our previous work and based on the approximation of the BO/bond length data by an exponential function.<sup>13a</sup> In such approximation we used the BOs available in literature and obtained in quantum chemistry calculations. It is

clear that such approach seems the most preferable nowadays. However, the M-Z bonding in the centered clusters is often represented by such heterometallic combinations like Co/Zr, Ni/Sc, Fe/Gd *etc.*, for which the BOs calculations are still very rare or completely absent. In addition, the problematic point of this approach is a high dispersion of the data obtained for the same bonds by different authors and various calculation techniques. As a result, valuable BV parameters for any atomic pairs can be obtained only from numerous DFT data, with a wide range of interatomic distances.<sup>13a</sup>

The third method is based on the BO conservation principle (see Eqs 1-3 of the main text).<sup>13b</sup> The key assumption of this approach is that the total BVS of the M atom in the  $M_n$ -cluster should be equal or very close to the value predicted by the MO structure. In particular, it can be equal to the number of valence electrons of the M atom, e.g., 3 for Sc, Y or Gd and 4 for Zr in the respective clusters. As was shown previously,<sup>13b</sup> such assumption is valid for the M-atoms in most of cluster compounds stabilized by outside ligands, but, to our knowledge, it was never proved for the centered clusters. Moreover, since each of the three approaches to determine the BV parameters has its problematic points, it was important to verify their validity by comparing the results of these methods.

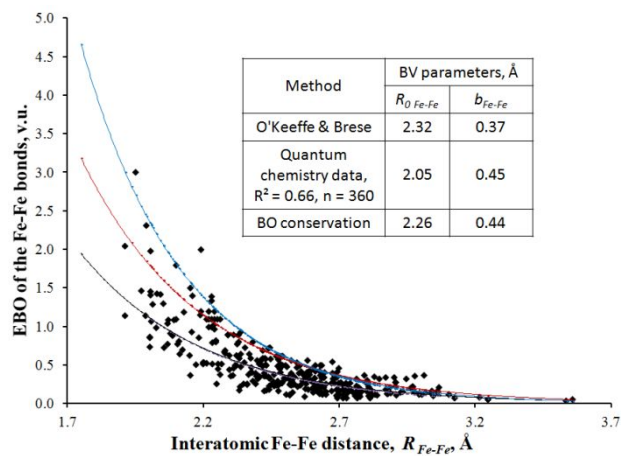
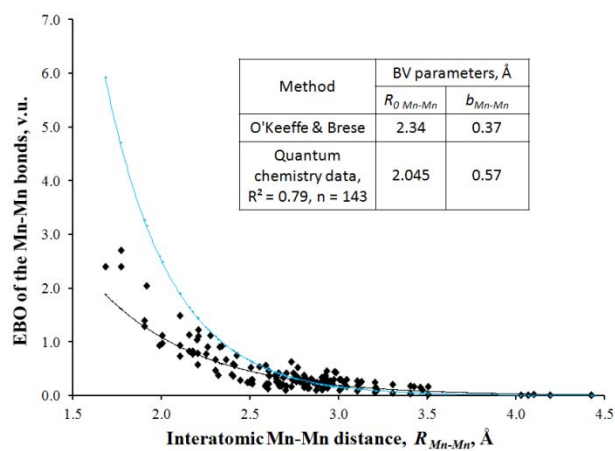
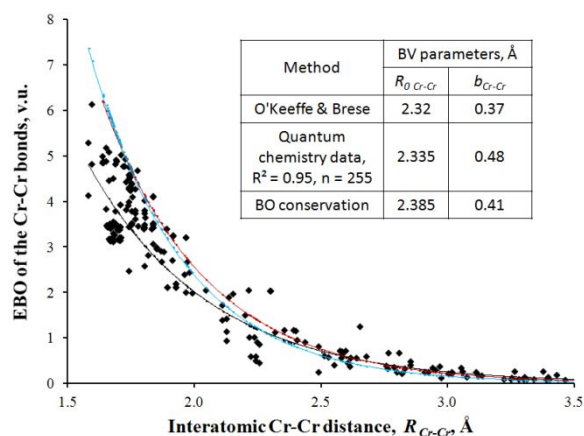
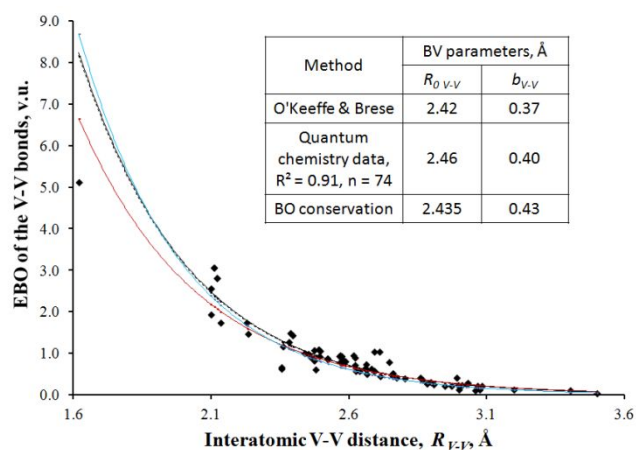
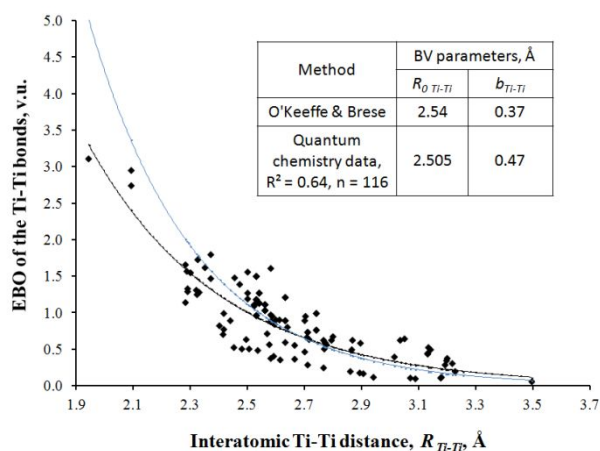
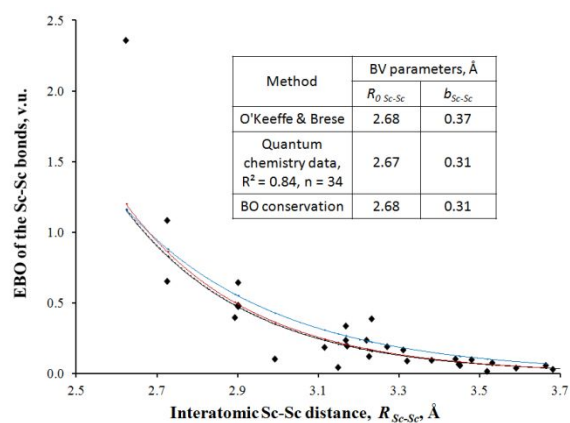
Figure S2 presents the exponential curves, which were obtained by different methods for the M-M bonds, and respective BV parameters (found by Eq 2 of the main text). As can be seen, for most of the M-M pairs, the three curves are close to each other; differences between them not exceeding the dispersion of the BOs calculated by DFT methods. Consequently, these parameters should ensure a proper bonding analysis for any complex compounds with respective metal-metal bonds. However, in some cases the distinctions in the curves are more pronounced, and respective changes were introduced in the BV parameters used in this work (Table S1).

To illustrate our reasoning in the choice of the BV parameters, Figure S3a compares the exponential curves and the BV parameters calculated by universal method with those obtained from quantum chemistry data for the Be-Be bonds. In spite of the high dispersion of the quantum chemistry data, it is clear that the prediction by O’Keeffe & Brese gives underestimated values of the BV parameters for these bonds. Since the same values of  $r_{Be}$  and  $c_{Be}$  should be used in the calculation by Eq S1 for the Zr-Be pair, we can expect that the predicted BV parameters for this pair will be also underestimated by the universal method. Thus, it seems logical that the best

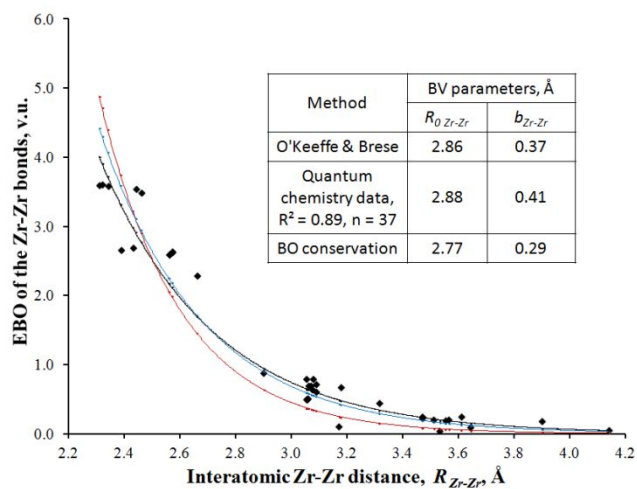
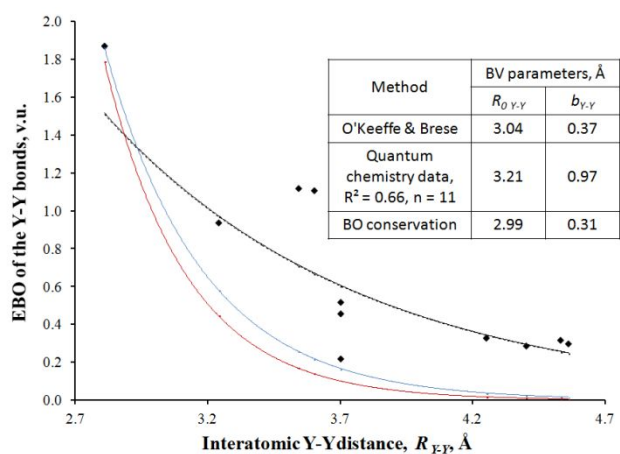
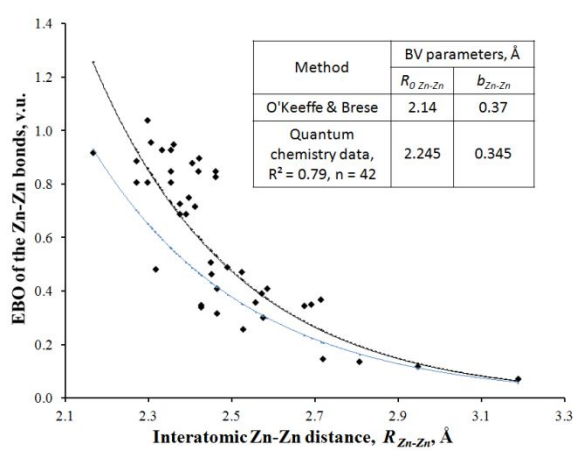
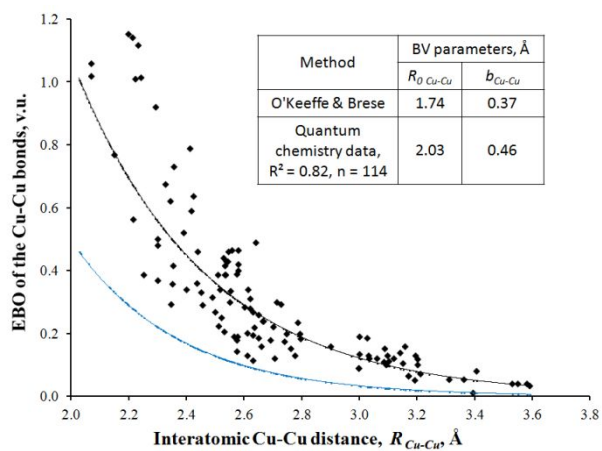
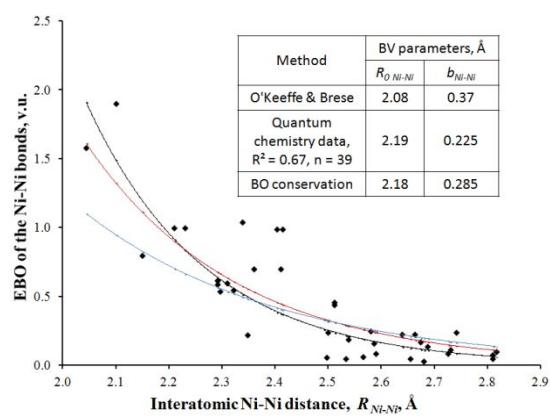
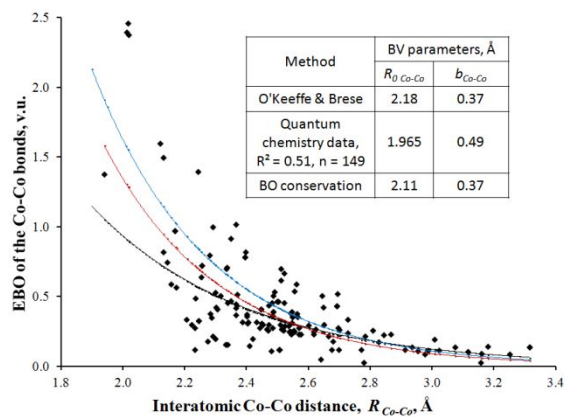
results for the cluster compounds with Zr-Be bonds are produced with the BV parameters based on the BO conservation principle, which are higher than the universal ones (red line in Fig. S3b). Quantum-chemically derived BV parameters are instead not available for the Zr-Be pair. For comparison, Figure S3b presents also the BV parameters for the Zr-Zr and Be-Be bonds, obtained through the BO conservation principle (Zr-Zr) and through the quantum chemistry data (Be-Be). As expected, the Zr-Be bonds have intermediate BV parameter values.

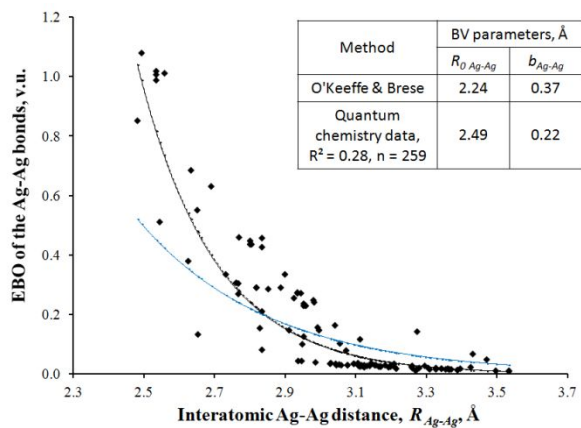
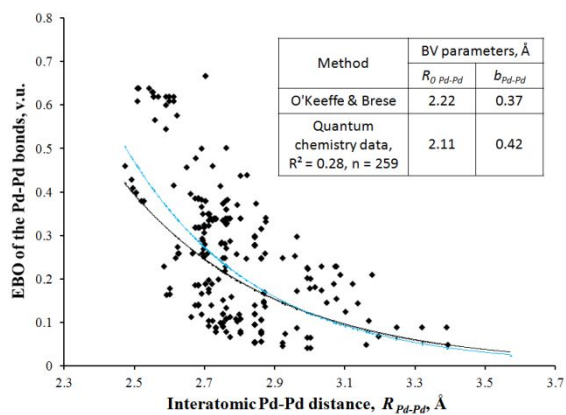
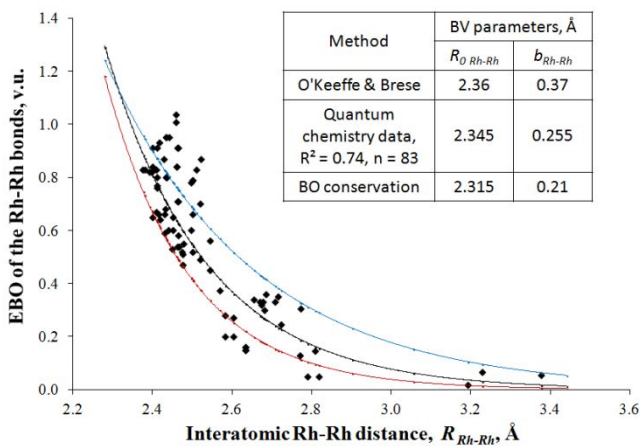
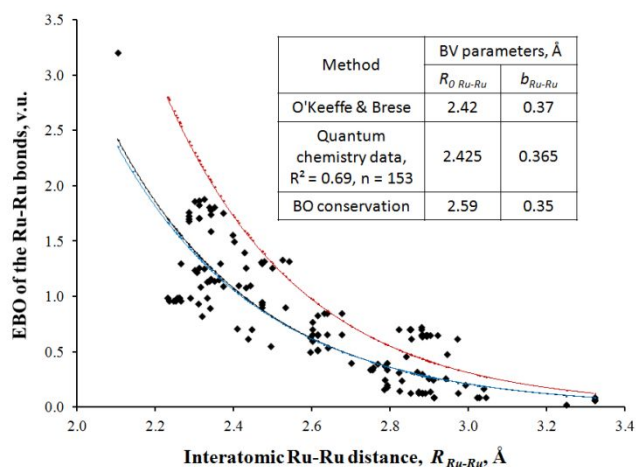
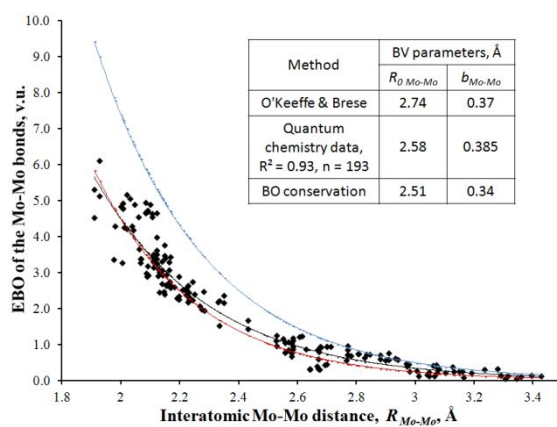
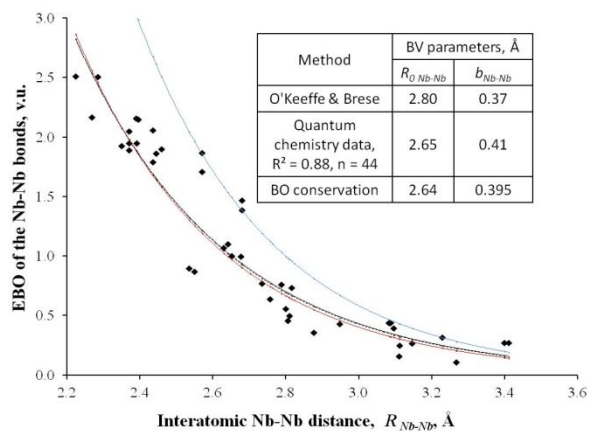
In contrast to the Be-Be bonds, the BV parameters of the B-B bonds obtained by O’Keeffe & Brese and DFT approaches are very close to each other (Figure S4). So, for the Zr-B and Sc-B bonds it is reasonable to use the BV parameters proposed by O’Keeffe & Brese (taking into account that the DFT data are absent or very poor for these atom pairs).

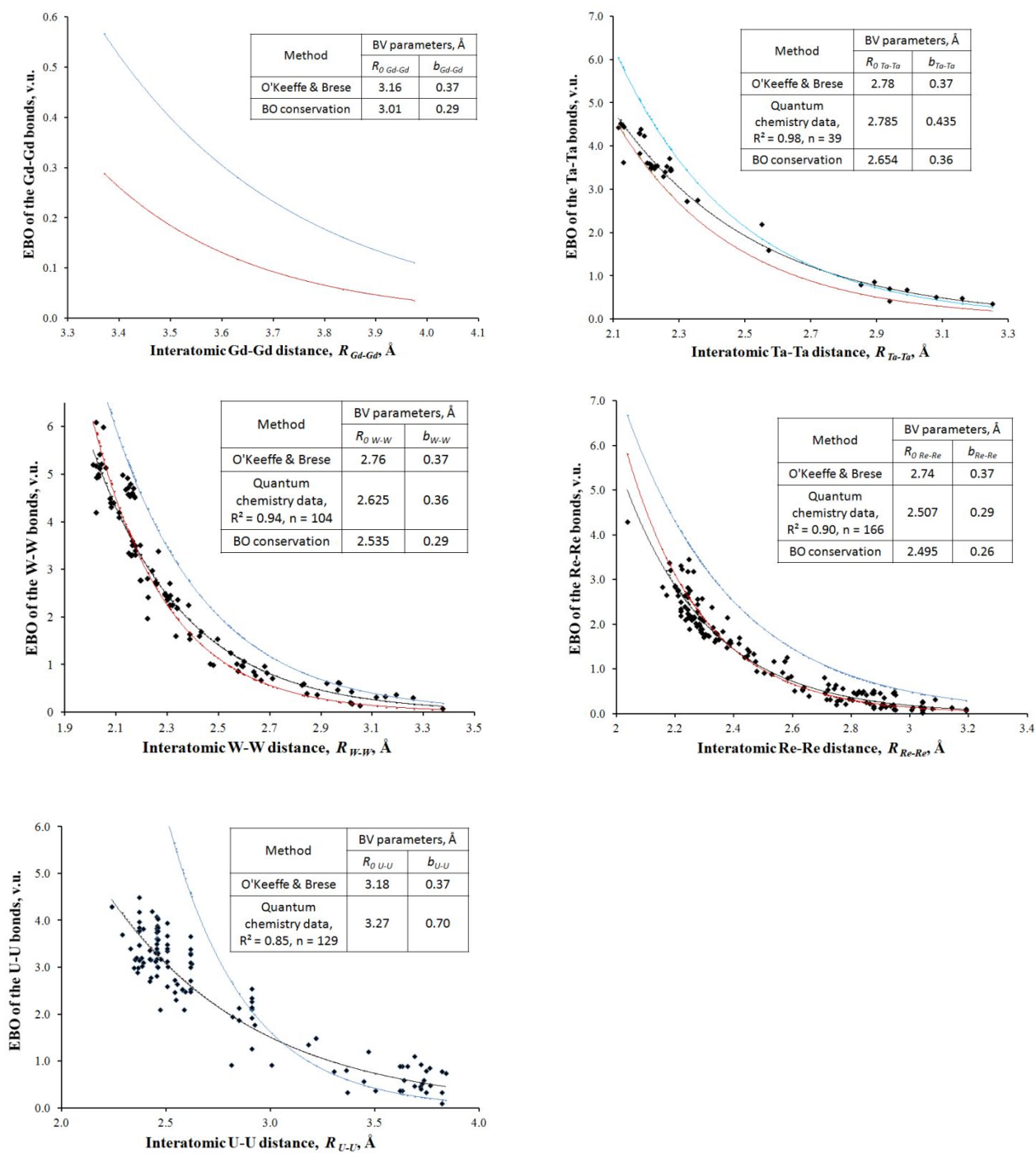
Another example is the choice of the BV parameters in the case of Zr-Z bonds with Z represented by such TMs like Mn, Fe, Co and Ni. These parameters obtained firstly by the universal method were fitted to satisfy the requirement of the total BVS close to 4 for the Zr atoms, i.e., they were finally established based on the BO conservation principle. Figure S5 presents the fitting of the BV parameters for the Zr-Co pair, for which there are also a few quantum chemistry data. As can be seen, all three methods (DFT, O’Keeffe & Brese and BO conservation) provide relatively close values of the BV parameters for such pairs.



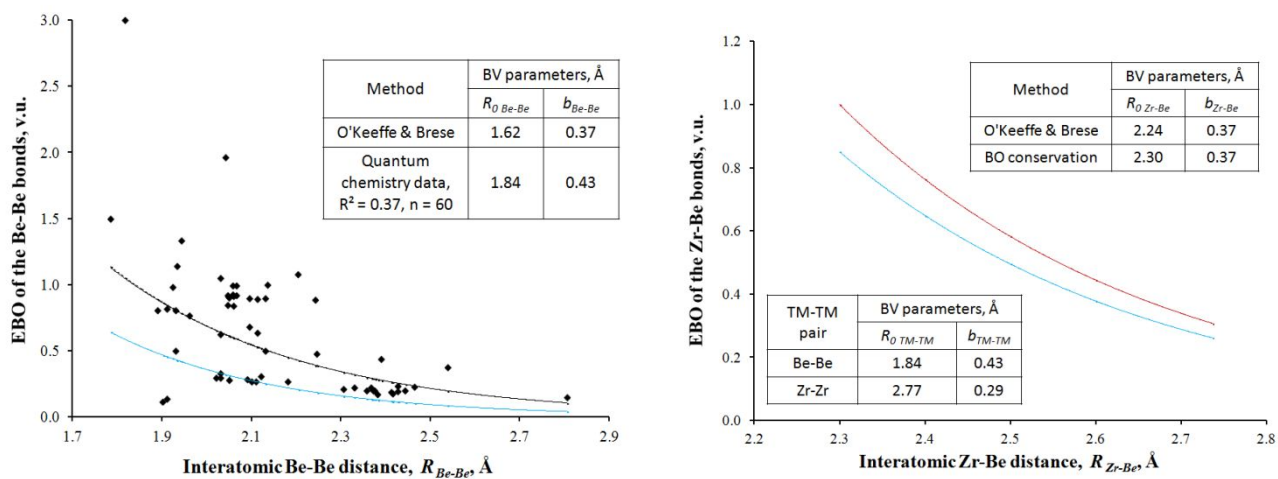




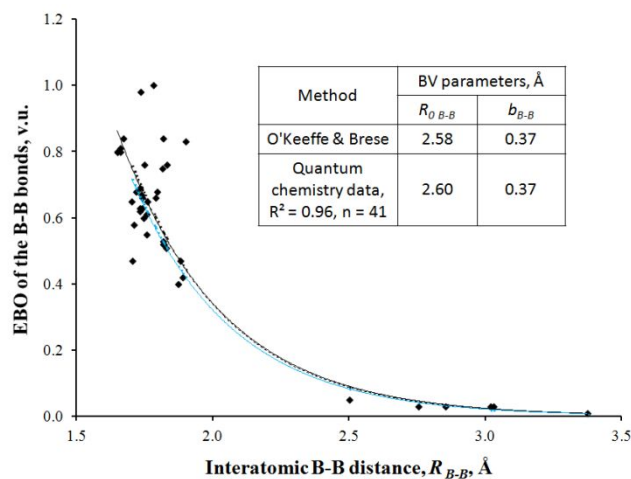




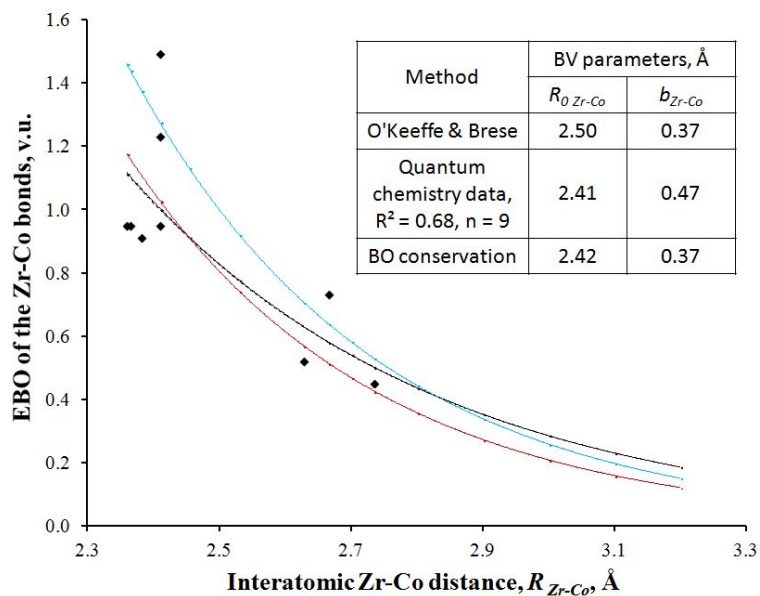
**Figure S2.** Exponential relationships between the effective bond orders (EBOs) of the M-M bonds and the respective interatomic distances. The black, blue and red curves are obtained based on DFT (see the references in our previous work<sup>16</sup>), O'Keeffe & Brese<sup>15</sup> and BO conservation approaches, respectively.



**Figure S3.** Exponential relationships between the effective bond orders (EBOs) of the Be-Be (a) and Zr-Be (b) bonds and the respective interatomic distances. The black, blue and red curves are obtained based on DFT, O'Keeffe & Brese<sup>15</sup> and BO conservation approaches, respectively. The references on the DFT data for the Be-Be bonds can be found in ref.<sup>17</sup>.



**Figure S4.** Exponential relationships between the effective bond orders (EBOs) of the B-B bonds and the respective interatomic distances. The black and blue curves are obtained based on the DFT and O'Keeffe & Brese<sup>15</sup> approaches, respectively. The references on the DFT data for the B-B bonds can be found in ref.<sup>18</sup>.



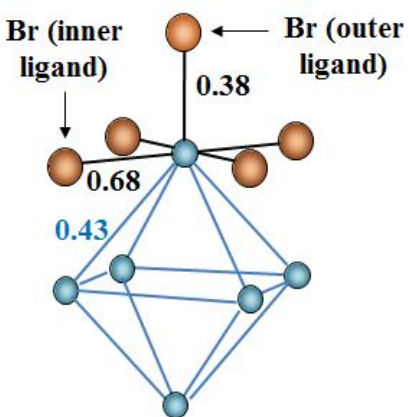
**Figure S5.** Exponential relationships between the effective bond orders (EBOs) of the Zr-Co bonds and the respective interatomic distances. The black, blue and red curves are obtained based on DFT (see the BO data in ref.<sup>19</sup>), O'Keeffe & Brese<sup>15</sup> and BO conservation approaches, respectively.

**a**  $\text{Cs}_2\text{EuNb}_6\text{Br}_{18}$

16 cluster valence electrons:

$$2+2+20-18$$

2 for Cs; 2 for Eu; 30 for Nb; 18  
for Br



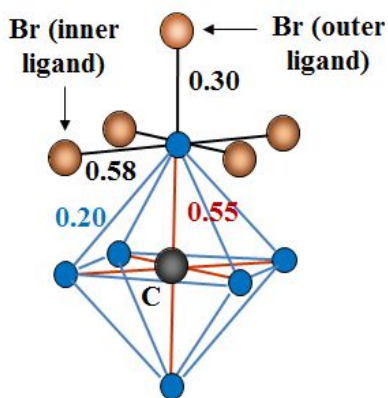
Bond	Bond length, Å	BV parameters, Å	Effective BO, v.u.	Formal BO, v.u.
Nb-Nb	2.967	$R_0 = 2.64;$ $b = 0.395$	0.437	0.667
	2.967		0.437	0.667
	2.974		0.429	0.667
	2.974		0.429	0.667
BVS Nb-Nb			1.733	2.667
Nb-Br	2.598	$R_0 = 2.45;$ $b = 0.37$	0.670	0.467
	2.603		0.661	0.467
	2.586		0.692	0.467
	2.592		0.681	0.467
	2.804		0.384	0.467
BVS Nb-Br			3.089	2.333
Total BVS <sub>Nb</sub>			4.822	5.000

**b**  $\text{Cs}_3(\text{CZr}_6)\text{Br}_{15}$

16 cluster valence electrons:

$$3+4+24-15$$

3 for Cs; 4 for C; 24 for Zr; 15  
for Br

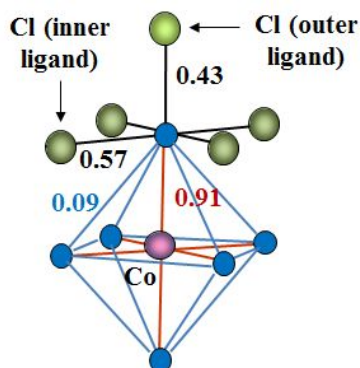


Bond	Bond length, Å	BV parameters, Å	Effective BO, v.u.	Formal BO, v.u.
Zr-Zr	3.228	$R_0 = 2.77;$ $b = 0.29$	0.206	0.333
	3.228		0.206	0.333
	3.239		0.198	0.333
	3.239		0.198	0.333
BVS Zr-Zr			0.809	1.333
Zr-Br	2.671	$R_0 = 2.48;$ $b = 0.37$	0.597	0.400
	2.681		0.581	0.400
	2.687		0.572	0.400
	2.688		0.570	0.400
	2.920		0.304	0.400
BVS Zr-Br			3.043	2.000
Zr-C	2.286	$R_0 = 2.103;$ $b = 0.305$	0.549	0.667
Total BVS <sub>Zr</sub>			3.982	4.000



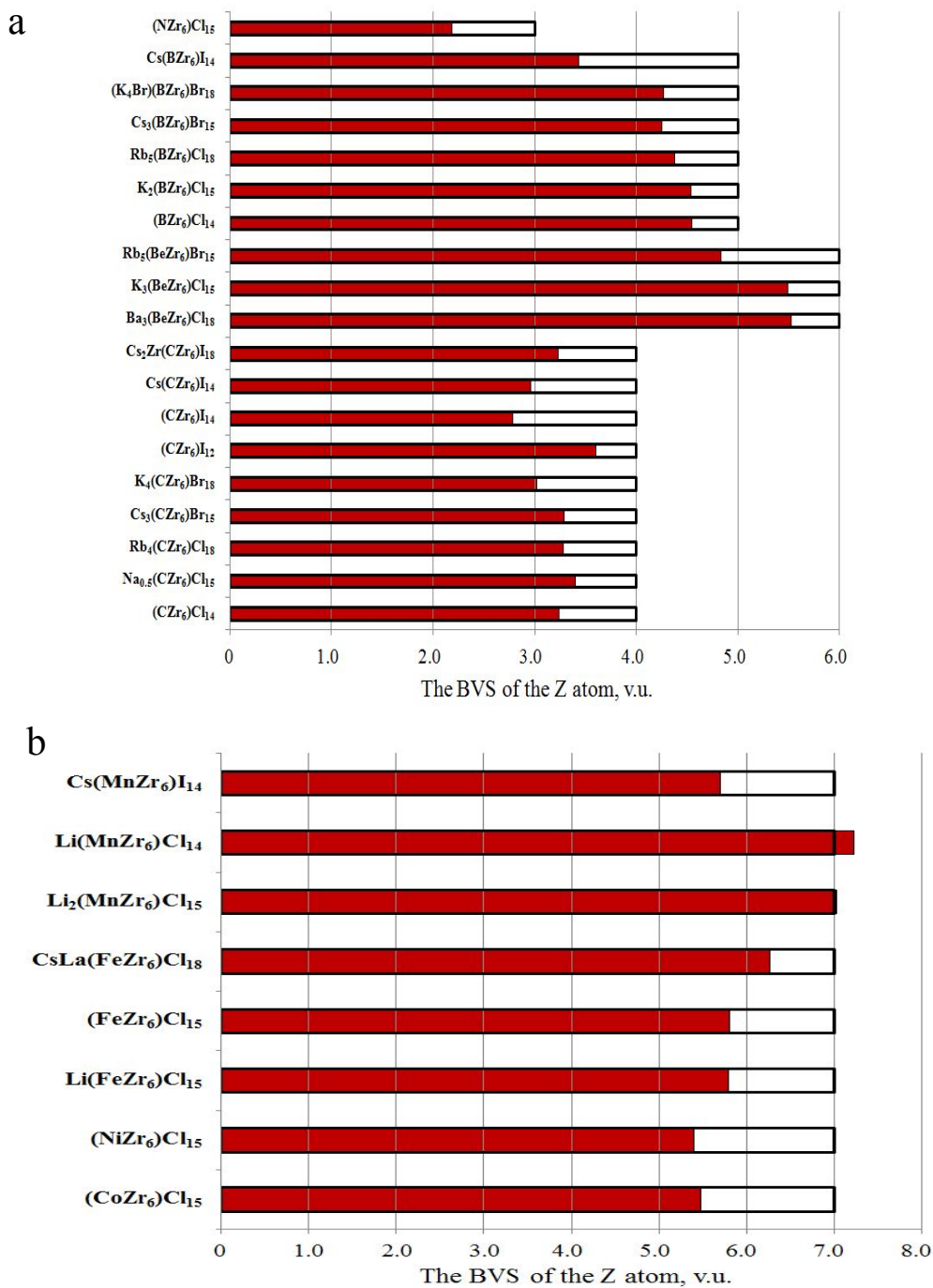
**C**      **(CoZr<sub>6</sub>)Cl<sub>15</sub>**

18 cluster valence electrons:  
9+24-15  
9 for Co; 24 for Zr; 15 for Cl



Bond	Bond length, Å	BV parameters, Å	Effective BO, v.u.	Formal BO, v.u.
Zr-Zr	3.471 3.471 3.471 3.471	$R_0 = 2.77;$ $b = 0.29$	0.089 0.089 0.089 0.089	0.083 0.083 0.083 0.083
BVS Zr-Zr			0.357	0.333
Zr-Cl	2.536 2.536 2.536 2.536 2.639	$R_0 = 2.33;$ $b = 0.37$	0.573 0.573 0.573 0.573 0.434	0.500 0.500 0.500 0.500 0.500
BVS Zr-Cl			2.726	2.500
Zr-Co	2.454	$R_0 = 2.42;$ $b = 0.37$	0.912	1.167
Total BVS <sub>Zr</sub>			3.995	4.000

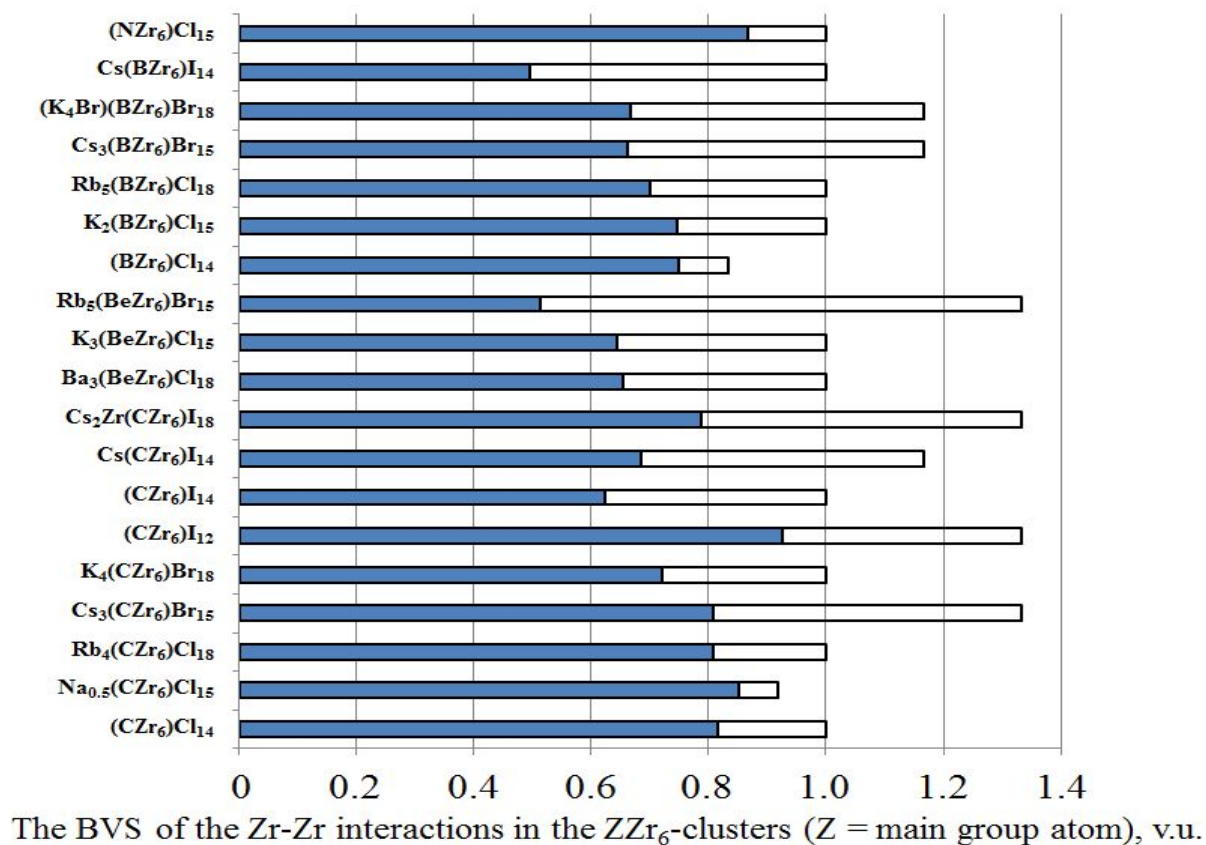
**Figure S6.** Typical examples of the BO calculation for the M atom in the M<sub>n</sub>-clusters. M = Nb (in light blue) in (a) and Zr (in blue) in Cs<sub>3</sub>(CZr<sub>6</sub>)Br<sub>15</sub> (b) and (CoZr<sub>6</sub>)Cl<sub>15</sub> (c) (Structural data of ref.<sup>20</sup> for Nb and ref.<sup>21</sup> for Zr). The numbers near the bonds are their effective BOs.



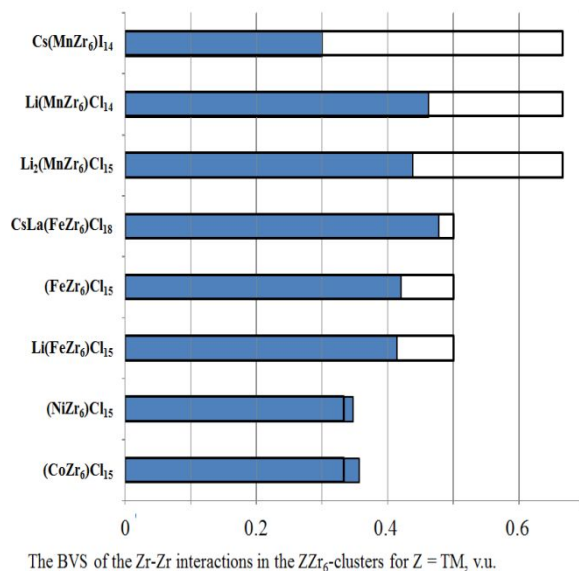
**Figure S7.** Comparison between the formal (the black borders) and the effective (in red) valences of Z atoms in Zr<sub>6</sub>-cluster compounds: a - Z is a main group atom: C, Be, B and N, b - Z is a transition metal atom: Mn, Fe, Co and Ni. Structural data are taken from ref.<sup>21-22</sup>



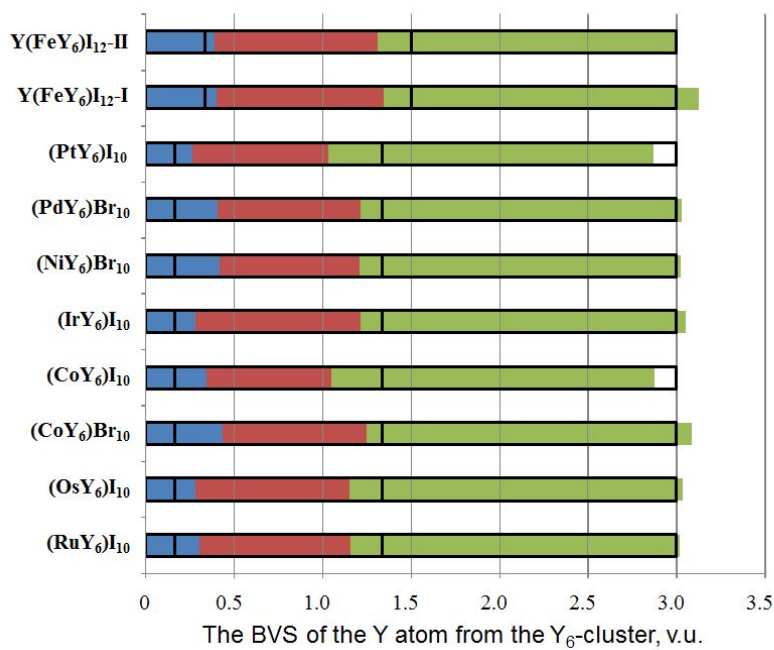
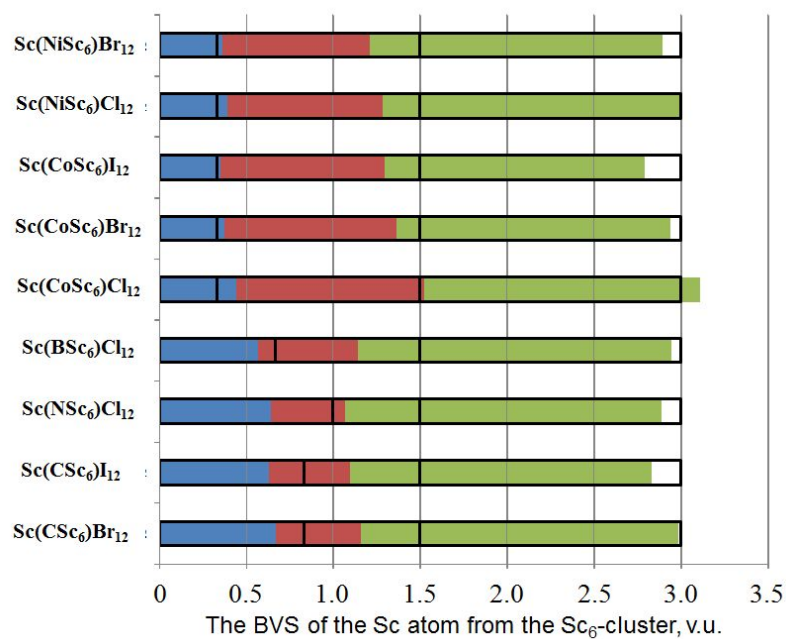
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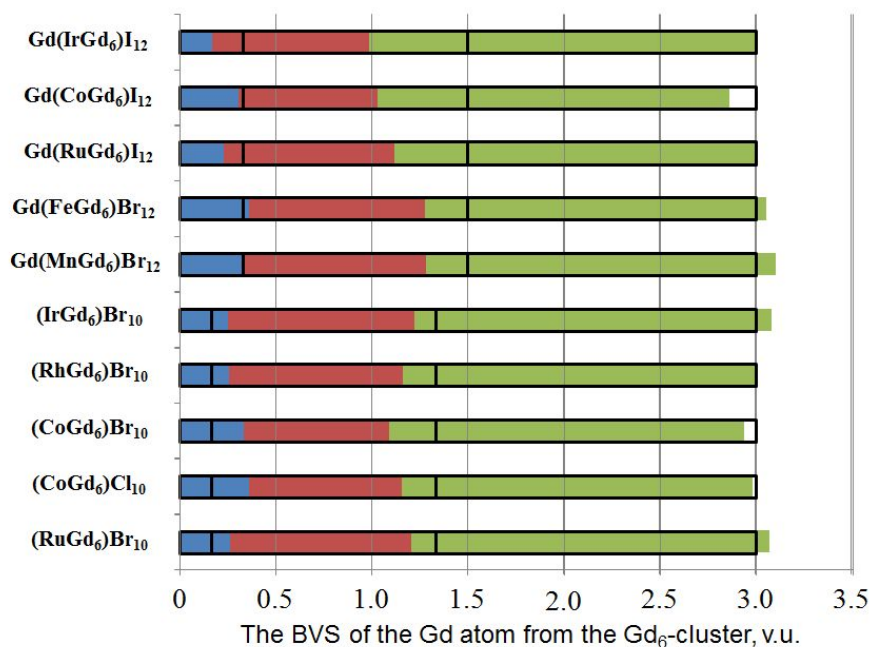


b



**Figure S8.** Comparison between the formal (the black borders) and the effective (in blue) bond valences of the Zr-Zr bonds in  $\text{Zr}_6$ -cluster compounds: a - clusters with  $Z$  presented by main group atom: C, Be, B and N, b - clusters with  $Z$  presented by transition metal atom: Mn, Fe, Co and Ni.





**Figure S9.** Comparison between the effective and formal BVSs of the Sc, Y and Gd atoms in respective cluster compounds. The partial BVS of the M-M (M = Sc, Y or Gd), M-Z and M-L bonds are in blue, red and green, respectively. The black borders (vertical black thick lines) mark the formal values. The structural data used in the calculations are taken from ref.<sup>23</sup> for the Sc<sub>6</sub>-clusters, refs.<sup>23d, 23e, 24</sup> for the Y<sub>6</sub>-clusters and refs.<sup>23d, 25</sup> for the Gd<sub>6</sub>-clusters.

Table S1. Bond valence parameters used in this work.

N	Bond	BV parameters, Å		N	Bond	BV parameters, Å	
		$R_{0ij}$	$b_{ij}$			$R_{0ij}$	$b_{ij}$
1	Sc-Sc	2.68	0.31	21	Zr-Zr	2.77	0.29
2	Sc-B	2.12	0.37	22	Zr-B	2.20	0.37
3	Sc-Br	2.38	0.37	23	Zr-Be	2.30	0.37
4	Sc-C	2.02	0.37	24	Zr-Br	2.48	0.37
5	Sc-Cl	2.23	0.37	25	Zr-C	2.103	0.305
6	Sc-Co	2.41	0.37	26	Zr-Cl	2.33	0.37
7	Sc-I	2.59	0.37	27	Zr-Co	2.50	0.37
8	Sc-N	1.98	0.37	28	Zr-Fe	2.44	0.37
9	Sc-Ni	2.36	0.37	29	Zr-I	2.69	0.37
				30	Zr-Mn	2.46	0.37
10	Y-Y	2.99	0.31	31	Zr-N	1.98	0.29
11	Y-Br	2.55	0.37	32	Zr-Ni	2.45	0.37
12	Y-Co	2.53	0.37				
13	Y-Fe	2.60	0.37	33	Gd-Gd	3.01	0.29
14	Y-I	2.77	0.37	34	Gd-Cl	2.41	0.40
15	Y-Ir	2.68	0.37	35	Gd-Co	2.54	0.37
16	Y-Ni	2.53	0.37	36	Gd-Br	2.56	0.40
17	Y-Os	2.65	0.37	37	Gd-Fe	2.59	0.37
18	Y-Pd	2.54	0.37	38	Gd-I	2.78	0.40
19	Y-Pt	2.62	0.37	39	Gd-Ir	2.70	0.37
20	Y-Ru	2.62	0.37	40	Gd-Mn	2.63	0.37
				41	Gd-Rh	2.66	0.37
				42	Gd-Ru	2.67	0.37

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