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Divalent Metals Can Reside on Bonds in Fullerenes†

Xuejiao Gao,[ab] Baoyun Sun,[b] Yuliang Zhao,[b] Bo-zhen Chen*[a] and Xingfa Gao*[b]

All data present in this study were computed using the at least two methods: the B3LYP density functional in conjugation with the 6-31G(d) basis for C and CEP-121G basis set and pseudopotential for metals (B3LYP/6-31G*~CEP-121G); the M062X density functional in conjugation with the 6-31G(d) basis for C and SDD basis set and pseudopotential for metals (M062X/6-31G*~CEP-SDD). The M062X/6-31G*~SDD and B3LYP/6-31G*~CEP-121G methods produce consistent results but one exception. The B3LYP/6-31G*~CEP-121G calculations suggest the existence of two energy minima for $Gd@C_{60}$: that with Gd above the hexagonal ring (**1**) and that with Gd above a 6/6 bond (**1b**). In contrast, the M062X/6-31G*~SDD calculations suggest the existence of one minimum **1**—the bond-bridging minimum **1b** does not exist in the potential energy surface at the level of M062X/6-31G*~SDD theory.

Orbital analysis suggest that **1b** has a divalent ionic structure $Gd^{2+}@C_{60}^{2-}$, which is different from that of **1** $Gd^{3+}@C_{60}^{3-}$. To investigate the reason for the different performances of the B3LYP/6-31G*~CEP-121G and M062X/6-31G*~SDD methods, we have calculated the ground state electronic structure for Gd^{2+} using four methods: B3LYP/SDD, M062X/SDD, B3LYP/CEP-121G and M062X/CEP-121G. It has experimentally determined that Gd^{2+} has a high-spin configuration of $4f^75d^1$ at ground state (H. A. Buskes and J. D. Cashion, *J. Phys. Colloques* **1974**, *35*, C6-221-C6-223). The M062X/SDD and B3LYP/SDD methods predict that Gd^{2+} has the high-spin configuration of $4f^76s^1$ at ground state. In contrast, the M062X/CEP-121G and B3LYP/CEP-121G methods predict that Gd^{2+} has the low-spin configuration of $4f^8$ at ground state. Therefore, the CEP-121G basis set and pseudopotential overestimates the spin pairing energy, which induces two electrons to occupy the same f orbital. Namely, the divalent structure $Gd^{2+}@C_{60}^{2-}$ located with the B3LYP/6-31G*~CEP-121G method is an artefact caused by the CEP-121G basis set and pseudopotential, which overestimates the spin paring energy of Gd's 4f orbital and prohibits the transfer of Gd's f electron to C_{60}. Although the use of SDD basis set and pseudopotential also predicts a different configuration for Gd^{2+} compared with that determined by experiment ($4f^76s^1$ *vs.* $4f^76d^1$), it will not significant influence the results about the trivalent structure $Gd^{3+}@C_{60}^{3-}$.

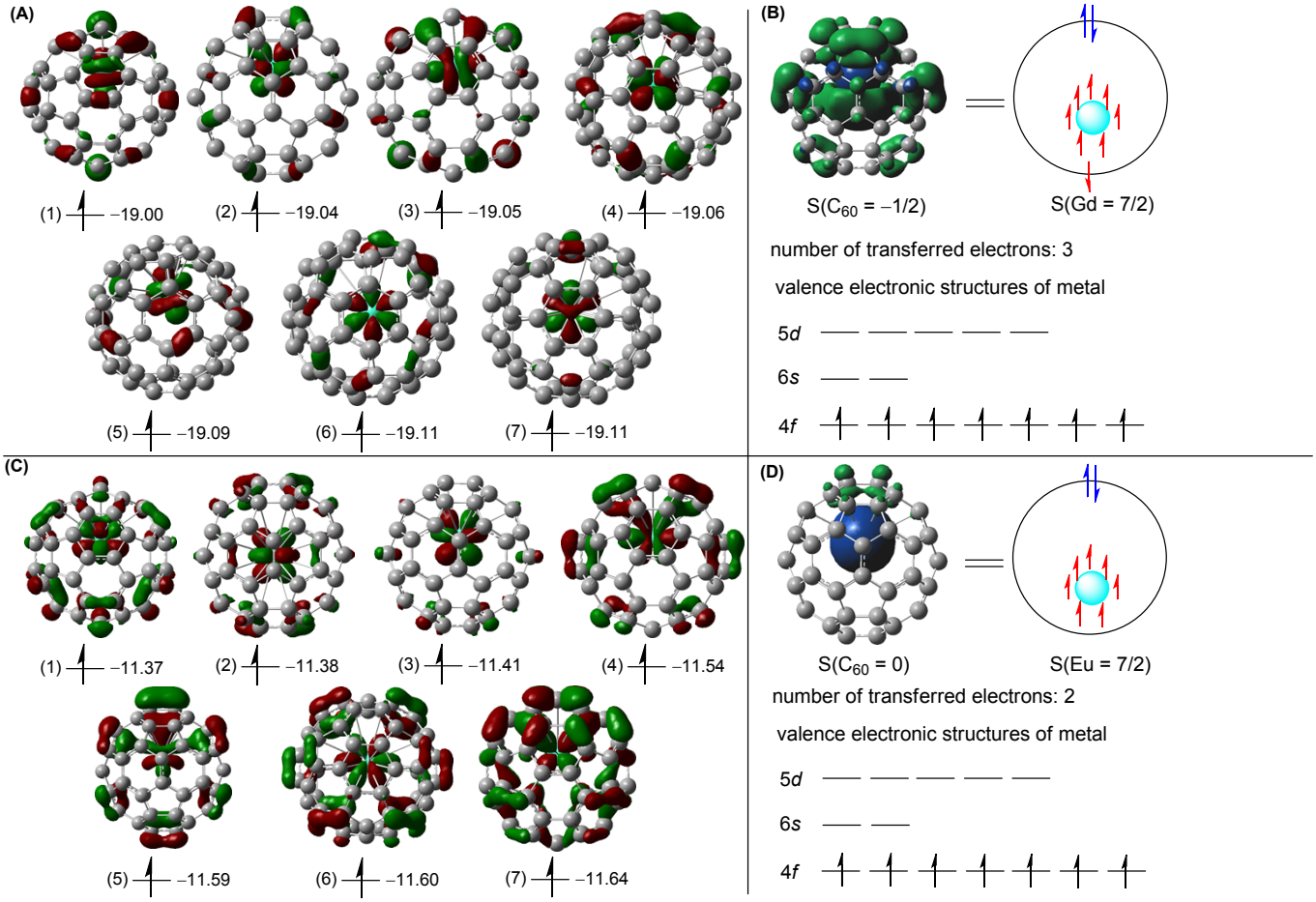

Fig. S1. Selected molecular orbitals of **1** (A) and **2** (C) (isovalue = 0.02) and spin density distributions of **1** (B)and **2** (D). In (A) and (C), the energies (in eV) of the orbitals are labeled. In (B) and (D), the spins (*S*) on the carbon cages and the metals and the number of transferred electrons are marked. The calculations were performed using the M062X/6-31G*~SDD method.

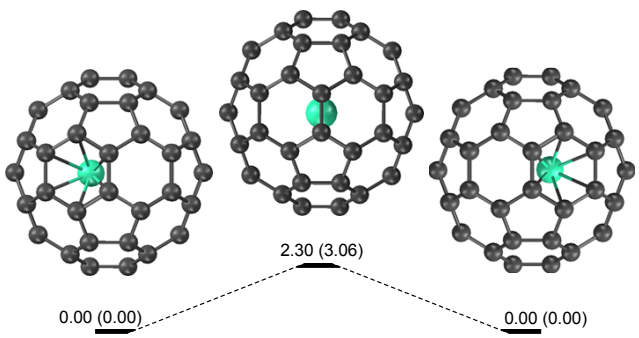

Fig. S2. Reaction energy profile for Gd@C_{60} **1** to transforms to its nearest symmetrically equivalent structure. Relative energies and Gibbs free energy (in parentheses) are marked with a unit of kcal/mol. The calculations were performed using the M062X/6-31G*~SDD method.

Table S1. Distances from metals to carbons in Yb@C_{80}, Yb@C_{82} and Yb@C_{84} [a] calculated with two different methods.

site	*d* (Å)		site	*d* (Å)		site	*d* (Å)	
	B3LYP/6-31G* ~CEP-121G	**M062X/6-31G* ~SDD**		**B3LYP/6-31G* ~CEP-121G**	**M062X/6-31G* ~SDD**		**B3LYP/6-31G* ~CEP-121G**	**M062X/6-31G* ~SDD**
3a			**3b**			**3c**		
a	2.5363	2.5172	a	2.4764	2.4635	a	2.5593	2.5539
b	2.7099	2.6986	b	2.6051	2.5612	b	2.6823	2.6786
c	2.9770	2.7965	c	2.5898	2.5901	c	2.8852	2.8778
d	2.6519	2.6243	d	2.8137	2.8351	d	2.6873	2.6811
e	2.8130	2.7748	e	2.8421	2.8305	e	2.8959	2.8831
			f	2.8912	2.8293			
4			**5a**			**5b**		
a	2.5975	2.5847	a	2.4722	2.4600	a	2.5095	2.4859
b	2.5693	2.5583	b	2.5316	2.5119	b	2.4940	2.4739
c	2.6031	2.5920	c	2.8937	2.8757	c	2.6498	2.6544
d	2.5983	2.5847	d	2.6281	2.6134	d	2.6397	2.6627
e	2.5732	2.5587	e	2.8641	2.8492	e	2.7401	2.6673
f	2.6064	2.5925	f	2.9257	2.9039	f	2.7806	2.7172
			g	2.7876	2.7635			
			h	3.2789	3.2537			
			i	3.5338	3.5124			
6			**7a**			**7b**		
a	2.5056	2.4892	a	2.5723	2.5788	a	2.5735	2.5440
b	2.7371	2.7142	b	2.6013	2.5903	b	2.6065	2.6786
c	2.8942	2.8683	c	2.6065	2.5765	c	2.6127	2.5565
d	2.6357	2.6164	d	2.5912	2.5600	d	2.7142	2.8865
e	2.8095	2.7870	e	2.6019	2.5885	e	2.7819	2.6416
			f	2.5877	2.5944	f	2.8376	2.9286

Table S2. Distances from metals to carbons in Gd@C_{60}, Eu@C_{60} calculated with the M062X/6-31G*~SDD method.

site	*d* (Å)		site	*d* (Å)	
	6-31G*	6-311G*		6-31G*	6-311G*
1			**2**		
a	2.6366	2.6091	a	2.6973	2.6956
b	2.4736	2.5993	b	2.7927	2.7915
c	2.3912	2.5886	c	2.9252	2.9233

Table S3. Relative energies (kcal/mol) and relative Gibbs free energies (in parentheses, kcal/mol) for Yb@C_{2n} isomers calculated with different methods.

	isomers	B3LYP/6-31G*~ CEP-121G[a]	B3LYP/6-31G*~ SDD[b]	PBEPBE/6-31G*~ CEP-121G	M062X/6-31G*~ SDD
Yb@C_{80}	**3a**	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
	3b	5.72 (5.32)	5.48 (7.89)	6.64 (6.16)	7.02 (6.19)
	3c	5.89 (4.89)	6.38 (8.06)	4.32 (3.53)	7.53 (6.49)
Yb@C_{82}	**4**	4.28 (4.51)	4.20 (4.30)	3.94 (4.31)	3.46 (3.73)
	5a	2.13 (1.50)	2.11 (1.26)	2.69 (1.90)	0.86 (0.70)
	5b	2.18 (1.92)	2.18 (2.32)	2.62 (2.67)	1.21 (1.49)
	6	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Yb@C_{84}	**7a**	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
	7b	16.88 (16.26)	17.46 (14.73)	13.18 (12.98)	20.22 (20.23)

Table S4. Total Energies, Minimum Frequencies, Spin Multiplicities, Point Groups and Cartesian Coordinates Calculated for the EMFs Discussed in the

[a] The coordinate files are archived in the compressed file named "optimized structures.pdf" of the supporting information.

Structures	Total Energy (Hatree)	Minimum Frequency (cm^{-1})	Spin Multiplicity	Point Group Symmetry	Filename[a]
1a [Gd@C_{60} (hexagon)]	-2398.155046	37.39	7	C_s	1a.xyz
1b [Gd@C_{60} (6/6 bond)]	-2398.137355	32.59	7	C_{2v}	1b.xyz
2 [Eu@C_{60} (6/6 bond)]	-2382.153023	27.46	8	C_{2v}	2.xyz
3a [Yb@C_{80}-C_{2v}(3)]	-3295.976731	34.19	1	C_s	3a.xyz
3b [Yb@C_{80}-C_{2v}(3)]	-3295.967613	28.08	1	C_s	3b.xyz
3c [Yb@C_{80}-C_{2v}(3)]	-3295.967341	17.81	1	C_s	3c.xyz
4 [Yb@C_{82}-C_2(5)]	-3372.20926	17.47	1	C_1	4.xyz
5a [Yb@C_{82}-C_s(6)]	-3372.212679	9.03	1	C_s	5a.xyz
5b [[Yb@C_{82}-C_s(6)]	-3372.212594	13.37	1	C_1	5b.xyz
6 [Yb@C_{84}-C_2(13)]	-3372.216075	23.47	1	C_s	6.xyz
7a [Yb@C_{84}-C_2(13)]	-3448.433497	11.06	1	C_1	7a.xyz
7b [Yb@C_{84}-C_2(13)]	-3448.406593	21.56	1	C_1	7b.xyz
Ce@C_{60} (6/6 bond)	-2324.962869	39.42	3	C_{2v}	CeC_{60}_66_bond.xyz
Dy@C_{60} (6/6 bond)	-2435.522651	22.62	5	C_{2v}	DyC_{60}_66_bond.xyz
Er@C_{60} (6/6 bond)	-2480.460093	34.22	3	C_{2v}	ErC_{60}_66_bond.xyz
Ho@C_{60} (6/6 bond)	-2457.009617	34.25	4	C_{2v}	HoC_{60}_66_bond.xyz
La@C_{60} (hexagon)	-2317.646231	44.69	2	C_1	LaC_{60}_hexagon.xyz
Lu@C_{60} (hexagon)	-2563.484844	31.92	2	C_s	LuC_{60}_hexagon.xyz
Nd@C_{60} (6/6 bond)	-2343.411799	31.86	5	C_{2v}	NdC_{60}_66_bond.xyz
Pm@C_{60} (6/6 bond)	-2354.72442	17.09	6	C_{2v}	PmC_{60}_66_bond.xyz
Pr@C_{60} (6/6 bond)	-2333.485048	23.26	4	C_{2v}	PrC_{60}_66_bond.xyz
Sm@C_{60} (6/6 bond)	-2367.611021	35.69	7	C_{2v}	SmC_{60}_66_bond.xyz
Tb@C_{60} (6/6 bond)	-2415.922152	41	6	C_1	TbC_{60}_66_bond.xyz
Tm@C_{60} (6/6 bond)	-2505.995599	31.11	2	C_{2v}	TmC_{60}_66_bond.xyz
Yb@C_{60} (6/6 bond)	-2533.713865	35.48	1	C_{2v}	YbC_{60}_66_bond.xyz

Full citations for Refs. 74

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