Density functional calculations on 13-atom $Pd_{12}M$ (M = Sc–Ni) bimetallic clusters*

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The geometric structures, electronic and magnetic properties of the 3d transition metal doped clusters $Pd_{12}M$ (M = Sc–Ni) are studied using the semi-core pseudopots density functional theory. The groundstate geometric structure of the $Pd_{12}M$ cluster is probably of pseudoicosahedron. The I_h-$Pd_{12}M$ cluster has the most thermodynamic stability in five different symmetric isomers. The energy gap shows that $Pd_{12}M$ cluster is partly metallic. Both the absolutely predominant metal bond and very weak covalent bond might exist in the $Pd_{12}M$ cluster. The magnetic moment of $Pd_{12}M$ varies from 0 to 5 μ_B, implying that it has a potential application in new nanomaterials with tunable magnetic properties.

Keywords: transition metal, electronic properties, magnetic properties, density functional theory

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1. Introduction

Transition metal (TM) clusters have been widely used for developing new magnetic materials with large moments and new catalysts with high reactivity.[1] Recently, Xiang *et al.*[2] predicted that the icosahedral Ni_{13} is very stable and Kilcoyne *et al.*[3] simulated annealing study on the structural stability of Ni_{2-55} and performed an experimental electric dipole polarizability study for Ni_{12-58}. Their geometries are similar to those for the Pt_n (n = 13, 38, and 55) nanoclusters.[4] As is well known, Ni, Pd, and Pt are in the same group of the element periodic table. Therefore, Pd_n clusters should embody similar structural properties to those of Ni_n and Pt_n. To our expectation, Rogan *et al.*[5] predicted that the icosahedral symmetric Pd_{13} was a magic number cluster and had relatively high stability. Zhang and Wang[6] found that Pd_{13} favoured an encapsulated icosahedron structure, which encaged one Pd atom in the cage centre and was slightly more stable than others. Naturally, another correlated question is brought forward: if the central Pd atom is substituted by other TMs such as Sc, Ti, V, Cr, Mn, Fe, Co, and Ni to form some new bimetallic clusters, how will the electronic and magnetic properties be changed? This is a meaningful issue that should be taken into deeper consideration.

To the best of our knowledge, systematic investigations of the neutral Pd_{12} cluster doped by other 3d TM atom (TMA) ($Pd_{12}M$, with M from Sc to Ni) have not been reported. In this work, using density functional theory (DFT), we elucidate the TMA doped clusters $Pd_{12}M$ (M = Sc–Ni) to explore their geometric structures and electronic and magnetic properties. We aim to answer the following two questions: (1) what are the ground state structures of the $Pd_{12}M$ clusters? (2) What are the electronic and magnetic properties of the most stable $Pd_{12}M$ clusters?

2. Method and computational details

All the density functional calculations reported here are carried out using the Dmol^3 package.[7] Relativistic calculations are performed with scalar relativistic corrections to valence orbitals relevant to atomic bonding properties via a local

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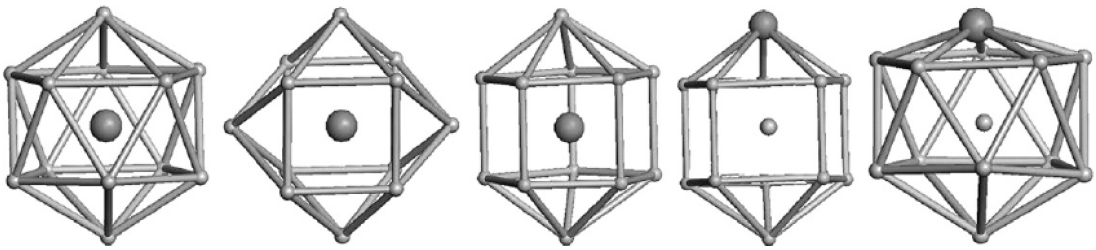
pseudopotential.[8] We adopt the generalized gradient approximation implemented in the exchange-correlation functional, BLYP, which is a combination of the exchange functional developed by Becke[9] with the gradient corrected correlation functional of Lee–Yang–Parr.[10] We use the double numerical precision with polarization (DNP) basis set[7] for our calculations. The DNP basis set is comparable to Gaussian 6-31G** basis set.[11] Electronic structure is obtained by solving the spin-polarized Kohn–Sham (KS) equations self-consistently. A Mulliken population analysis is made to obtain the effective charges and net spin populations on each atom. Self-consistent field procedures are carried out with a convergence criterion of 10^{-6} a.u. on the energy and electron density. Geometry optimizations are performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm[12] with a convergence criterion of 10^{-3} a.u. for the displacement and 10^{-5} a.u. for the energy. All calculations are performed in the absence of symmetry constraint and periodic boundary conditions.

There is no imaginary frequency for the structure reported here. In addition, for geometry optimization of each isomer, the spin multiplicity (SM) is considered to be at least 1, 3, 5 for even-electron clusters (Ti, Cr, Fe, Ni) and 2, 4, 6 for odd-electron clusters (Sc, V, Mn, Co). If the total energy decreases with the increase of SM, we will consider a higher spin state until the energy minimum corresponding to SM is reached. In order to test the reliability of our calculations, the Pd_2 dimer is firstly computed. The calculated results indicate that the Pd–Pd bond length (2.45 Å) accords well with the computational results of Valerio and Toulhoat[13] (2.53 Å) and Seminario *et al.*[14] (2.56 Å), but it is slightly smaller than the experimental value of 2.48 Å.[15] The binding energy (2.42 eV) is in close agreement with the experimental value (2.06 eV).[5] Therefore, the method used in this paper is reliable.

3. Results and discussion

3.1. Structure and stability

The results indicate that Pd_{13} favours an encapsulated icosahedron structure and that one Pd atom is confined in the cage centre.[5] As is well known, many possible isomers are reported for the 13-atom cluster. For instance, two geometries with I_h or O_h symmetry are considered as the starting configurations of $Sn_{12}M$ (M = Sc–Ni) clusters for optimizations.[6] Four isomers with I_h, D_{5h}, C_{5v}, and C_s symmetries for the 13-atom clusters $In_{12}X$ (X = Si, Ge, Sn) are considered by Liu *et al.*[16] Therefore, in order to find out the most stable structure, five probable geometries with I_h, D_{5h}, O_h, C_{5v}, and C_s symmetries are taken as the starting structures for $Pd_{12}M$ (M = Sc–Ni), which are shown in Fig. 1. The O_h structure is of a cuboctahedron, a compact portion of the fcc crystal lattice. The D_{5h} structure (namely, the decahedron structure) can be obtained from the icosahedral one by rotating the top pentagonal cap up to 36°. The C_{5v} structure is that the tetravalent atom is adsorbed on the vertex of the D_{5h} structure.



(a) $Pd_{12}M$-I_h (b) $Pd_{12}M$-O_h (c) $Pd_{12}M$-D_{5h} (d) $Pd_{12}M$-C_{5v} (e) $Pd_{12}M$-C_s

Fig. 1. Initial geometric structures of five different symmetric ((a) I_h, (b) O_h, (c) D_{5h}, (d) C_{5v}, and (e) C_s) clusters of $Pd_{12}M$ (M = Sc–Ni), where the big ball denotes the doped M atom, and the small ball the Pd atom.

Table 1 presents the relative energies ΔE of all the $Pd_{12}M$ (M = Sc–Ni) clusters. The ΔE is defined as the difference in energy between the considered structure and the lowest energy isomer. Obviously, the I_h isomer for eight $Pd_{12}M$ structures has the lowest energy. Our calculations show that all I_h–$Pd_{12}M$ clusters have different structural distortions owing to the Jahn–Teller effect. For the V dopant, the clusters can maintain the perfect I_h symmetry within 0.01 Å tolerance, while the clusters with Sc, Ti, and Fe dopants are more distorted. They can maintain the I_h symmetry only within 0.1 Å tolerance, whereas the

geometry optimizations for Cr, Mn, Co and Ni will be mostly distorted within 0.2 Å tolerance. Therefore, all the structures here can be regarded as being of pseudoicosahedron. The TMA is still situated in the cage centre, therefore, the structural distortion depends mainly on the doped TMA, analogous to the 3d-TMA doped clusters of Si[17] and Sn,[18] respectively.

Table 1. The ΔEs, DEs, and E_gs of five symmetric clusters $Pd_{12}M$ (M = Sc–Ni) (in units of eV).

		I_h	O_h	D_{5h}	C_{5v}	C_s
	ΔE	0.00	0.38	0.08	1.56	1.44
$Pd_{12}Sc$	DE	9.80	8.44	8.55	7.73	7.19
	E_g	0.07	0.16	0.15	0.16	0.16
	ΔE	0.00	0.26	0.39	2.24	0.57
$Pd_{12}Ti$	DE	10.61	9.52	9.35	7.98	9.07
	E_g	0.06	0.16	0.08	0.13	0.21
	ΔE	0.00	0.07	0.70	0.15	0.61
$Pd_{12}V$	DE	9.25	8.44	7.30	8.39	7.58
	E_g	0.12	0.09	0.15	0.26	0.11
	ΔE	0.00	0.30	0.02	0.24	1.99
$Pd_{12}Cr$	DE	6.26	5.71	5.44	5.71	3.81
	E_g	0.08	0.20	0.08	0.16	0.14
	ΔE	0.00	0.24	0.08	1.14	0.95
$Pd_{12}Mn$	DE	6.53	5.44	5.44	4.63	4.35
	E_g	0.07	0.12	0.14	0.02	0.14
	ΔE	0.00	0.05	0.33	2.53	1.31
$Pd_{12}Fe$	DE	7.62	6.53	5.99	5.67	5.17
	E_g	0.1	0.09	0.15	0.10	0.01
	ΔE	0.00	0.28	0.19	1.24	1.19
$Pd_{12}Co$	DE	5.44	5.99	5.44	4.90	8.44
	E_g	0.11	0.17	0.16	0.14	0.96
	ΔE	0.00	0.05	0.15	0.06	0.76
$Pd_{12}Ni$	DE	1.90	1.09	0.82	0.27	0.00
	E_g	0.13	0.11	0.14	0.15	0.13

Initially, the average length of Pd–Pd bonds in a $Pd_{12}M$ cluster is calculated, which can be defined as $R = \sum R_{ij}/n_b$, where R_{ij} is the bond length between i and j Pd atoms, lying within a distance not exceeding 15%[19] of the minimum distance of bulk Pd metal (2.75 Å), and n_b is the total bond number. The calculated average lengths of all Pd–Pd bonds in the $Pd_{12}M$ clusters are elongated by about 3.6%, 2.5%, 1.8%, 2.1%, 2.9%, 2.2%, 2.5%, and 2.2% compared with the average length of Pd–Pd bonds in the pristine Pd_{12} cluster. This indicates that the M doping draws the cage outward to some degree.

Table 1 also lists the doping energies (DEs) of $Pd_{12}M$ (M = Sc–Ni) clusters. The DE is defined as the total energy of $Pd_{12}M$ minus the sum of total energies of the Pd_{12} and the TMA.[20] If the DE is greater than zero, it means the reaction is exothermic.[20] In our calculation, all pseudoicosahedron $Pd_{12}M$ clusters have the positive DEs, therefore, the reactions to synthesize them are exothermic and favourable. Of them the I_h-$Pd_{12}M$ has the largest DE, indicating it is most stable of all.

Additionally, we compare the values of E_g shown in Table 1. The E_g is the energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), which is another useful quantity for examining the kinetic stability of a cluster.[21] A larger E_g corresponds to the high strength required to perturb the electronic structure. The computed value of E_g of I_h-Pd_{12} is 0.12 eV, indicative of its remarkable activity. While the values of E_g of all the isomers of doped $Pd_{12}M$ are all less than 1eV, indicating that all $Pd_{12}M$ clusters are partly metallic.

3.2. Frontier orbital properties

In quantum chemistry, the reactivity of a molecule can be correlated with its frontier orbitals. Commonly, the atom which is the main component of the HOMO should have the stronger ability for detaching electrons, whereas the atom which is the main component of the LUMO should be easier to gain electrons.[22] We present the HOMO and LUMO wavefunctions of $Pd_{12}M$ shown in Fig. 2, where the dark and light represent the negative and positive parts of the wave functions. It is observed that the HOMOs and LUMOs of $Pd_{12}M$ have almost no distribution on the TMA. Therefore, $Pd_{12}M$ (M = Sc–Ni) should have little ability to both gain and lose electrons.

Table 2 presents the values of the vertical ionization potential (VIP), vertical electron affinity (VEA), molecule electronegativity χ, chemical hardness η, and electrophilicity index ω of $Pd_{12}M$. The VIP is the energy difference between positively charged and neutral clusters. The VEA is evaluated by adding one electron to the neutral cluster in its equilibrium geometry and taking the difference between their total energies. The χ is identified by Parr[23] as the negative partial derivative of the energy E of an atomic or molecular system with respect to the number of electrons N for a constant external (i.e., due to the nuclei) potential v, written as $x = -(\frac{\partial E}{\partial N})_v$. Parr and Pearson,[24] on the basis of the Hard-Soft Acid-Base (HSAB) principle, identified the η as the second derivative of the energy

E with respect to the number of electrons N at a fixed external potential, i.e. $\eta = \frac{1}{2}(\frac{\partial^2 E}{\partial N^2})_\nu$. In a finite difference approximation using integer values for N, the expressions of the χ can be rewritten as the Mulliken-type formula: $x = (\mathrm{VIP} + \mathrm{VEA})/2$, while the η can be rewritten as $\eta = (\mathrm{VIP} - \mathrm{VEA})/2$.[25] The ω defined by Parr *et al.*[24] is the square of its electronegativity divided by its chemical hardness, that is, $\omega = \chi^2/(2\eta)$.

The calculated values of VIP and VEA of Pd_{12} are 5.93 and 1.98 eV, which are close, respectively, to the values of 6.18 and 2.03 eV computed by Chen *et al.*[26] It can be seen from the table that the values of VIP and VEA of $Pd_{12}M$ are very close to those of the Pd_{12} cluster, indicating that the M atom does not affect the ability to detach and attach electrons of the clusters. This is consistent with the frontier orbital analysis that the M occupies no component in the HOMOs and LUMOs of the clusters. Moreover, $Pd_{12}M$ clusters show almost the same values of χ, η and ω, indicating the electronegativity and chemical hardness of the Pd_{12} cluster are both little sensitive to the doped M atom.

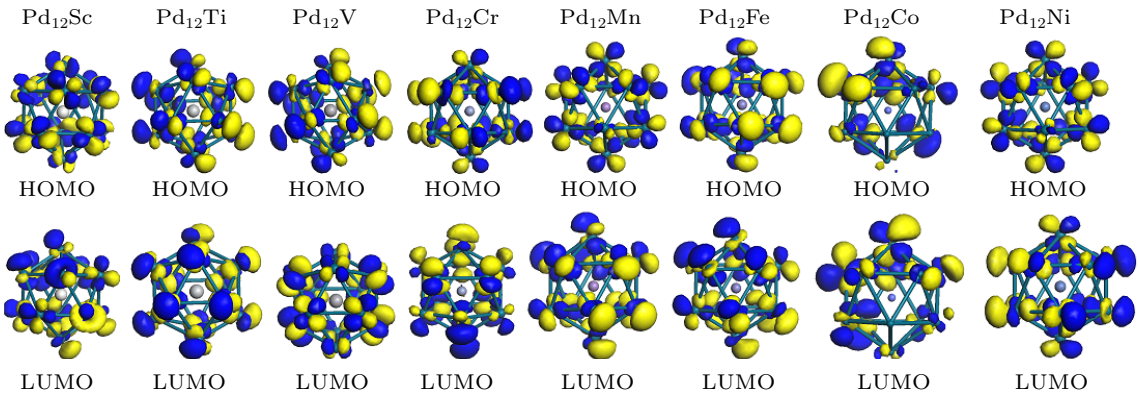


Fig. 2. The HOMO and LUMO wavefunctions of eight $Pd_{12}M$ clusters.

Table 2. Values of vertical ionization potential (VIP), vertical electron affinity (VEA), molecule electronegativity (χ), chemical hardness (η), electrophilicity index (ω), the magnetic moment of the M (M_{atom}), the magnetic moment of the twelve Pd atoms ($\mathrm{Pd_{total}}$), and the magnetic moment of the $Pd_{12}M$ clusters (M_{total}).

	Pd_{12}	$Pd_{12}Sc$	$Pd_{12}Ti$	$Pd_{12}V$	$Pd_{12}Cr$	$Pd_{12}Mn$	$Pd_{12}Fe$	$Pd_{12}Co$	$Pd_{12}Ni$
VIP/eV	5.93	5.91	5.93	6.12	5.98	5.92	5.85	6.07	5.94
VEA/eV	1.98	2.10	2.25	2.28	1.94	2.13	2.18	1.99	2.15
χ/eV	3.96	4.01	4.09	4.20	3.96	4.03	4.02	4.03	4.05
η/eV	1.98	1.91	1.84	1.92	2.02	1.89	1.84	2.04	1.90
ω/eV	3.96	4.21	4.55	4.59	3.88	4.30	4.39	3.98	4.32
$M_{\mathrm{atom}}/\mu_{\mathrm{B}}$	–	−0.07	−0.12	−0.27	−2.30	4.24	3.50	0.16	1.25
$\mathrm{Pd_{total}}/\mu_{\mathrm{B}}$	–	5.07	4.12	3.27	4.30	-5.24	6.50	2.84	6.75
$M_{\mathrm{total}}/\mu_{\mathrm{B}}$	–	5	4	3	2	1	2	3	0

3.3. Electron density

Total and deformed electron densities for $Pb_{12}Mn$ cluster are calculated and displayed as an example in Figs. 3(a) and 3(b) to elucidate the nature of the interaction between metal atoms. As is apparent from Fig. 3(a), spherical distribution appears around all metal atoms, which indicates that there should be a short covalent bond between metal atoms. To further clarify the interaction, deformed electron density shown in Fig. 3(b) is needed, which is equal to the total density subtracting the density of isolated atoms. The light isosurface represents the scenario of electron depletion, while the dark one denotes the electron accumulation. It is clear that more external electrons can be found in the spaces among the metal atoms instead of near the atoms, which is an obvious evidence for a metal bond. Moreover, the smallest Pd–M bond lengths of $Pd_{12}M$ are 2.73, 2.65, 2.67, 2.60, 2.70, 2.66, 2.62, and 2.60 Å, are larger, respectively, than the sum of the atom radius of Pd and M, i.e., 2.72, 2.60, 2.50,

2.46, 2.45, 2.45, 2.44 and 2.43 Å. Although a metal bond is absolutely predominant in the $Pd_{12}Mn$ cluster, the slight overlap can still be observed between central Mn atom and peripheral Pd atoms in $Pd_{12}Mn$, suggesting a covalent bond (even if very weak) might exist in the small-size clusters.

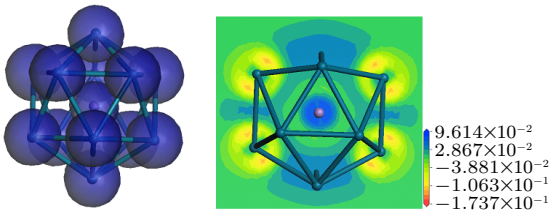


Fig. 3. (a) Total electron density of the $Pb_{12}Mn$ cluster (0.48 e/Å^3) and (b) deformed electron density of the $Pb_{12}Mn$ cluster.

3.4. Magnetic moment

Based on the optimized geometries, the magnetic moments of the M atom, twelve Pd atoms, and the $Pd_{12}M$ clusters are evaluated via the Mulliken charge population analysis (MPA) and the results are presented in Table 2. The magnetic moment is calculated from the formula $\mu = S_u - S_d$ where S_u and S_d are the numbers of majority and minority spins, respectively. The μ is in units of μ_B. As seen in this table, for all the $Pd_{12}M$ clusters, the total magnetic moment varies from to 5 μ_B. For the Sc (Ti, V, Cr, Mn) dopants, the local spin moments of Pd atoms are found to align antiferromagnetically to Sc (Ti, V, Cr, Mn). Moreover, it clearly shows that the total magnetic moment of the cluster is located mainly on the Pd site for Sc (Ti, V), whereas on both Pd and M sites for Cr (Mn). As to Fe (Co, Ni) dopants, there exists a strong ferromagnetic interaction between Fe (Co, Ni) and Pd atoms. The total magnetic moment of the cluster is mainly located both on the Pd and M sites. In fact, the previous study of the relative orientation of the magnetic moment of the encapsulated TMA to the magnetic moments of its neighbouring atoms also indicated that the magnetic interaction of the early transition metal is different from that of the late transition metal.[27]

4. Conclusion

In this paper, the groundstate geometries of the $Pd_{12}M$ clusters are probably of pseudoicosahedron. The I_h-$Pd_{12}M$ clusters have the most thermodynamic stability. All $Pd_{12}M$ clusters are partly metallic. $Pd_{12}M$ should have a small ability to gain and lose electrons. The absolutely predominant metal bond and very weak covalent bond might co-exist in the $Pd_{12}M$ cluster. $Pd_{12}M$ should have a potential application in new nanomaterials with tunable magnetic properties.

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