



New minima for the Pt₈ cluster

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ABSTRACT

We present a study on the structural and electronic properties of the Pt₈ cluster by performing density functional theory calculations in the framework of spin-polarized generalized gradient approximation. The structures, binding energies, HOMO–LUMO gaps, and vibrational frequencies of various isomers are calculated and compared with previously reported structures. In the literature, there are a number of different configurations proposed as the lowest energy isomer without a consensus. In our calculations it has been found that the most stable configuration is a triple tetragonal pyramid in the triplet state which supports one of the earlier studies. We have also identified seven new low-lying local minima for the Pt₈ cluster.

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1. Introduction

The quests for nanocatalysts, nanoscale information storage devices, nanospintronics, nanostructured materials and electronic devices are the main motivations for the study of metal clusters and nanoparticles for the last few decades [1–3]. Platinum, particularly, is not only the preferred oxidation and reduction catalyst for low-temperature polymer electrolyte membrane fuels cells, but also one of the most important ingredients in the catalysis of the CO, NO_x and hydrocarbons [4].

Although there are a number of theoretical, mostly density functional (DFT) studies on the geometrical structures and energetics of small platinum clusters [5–15], the results are often not consistent with each others and the most stable structures are still an issue in debate. The reasons for the inconsistencies of these calculations can be listed as the following: (i) inexactness of the chosen exchange–correlation functionals, (ii) incompleteness of the employed basis sets, (iii) insufficiency of the applied methods to search the global minimum. The complexity of the electronic structures of metal clusters contributes to all of these reasons and makes the achievement of a consensus to be more difficult. A few experimental studies on the vibrational and the electronic spectra of small platinum clusters consisting of 2–6 atoms [16–21] are not enough to solve the discrepancies.

In this work, we present the DFT studies of structural and electronic properties of the Pt₈ cluster to locate its possible minima and ground state. The previously proposed structures in the most recent studies are the following: Xiao and Wang [6] have found a cubic structure with 8 μ_B magnetic moment (M) in their plane

wave basis set calculations in 2004. Futschek et al. [9] have identified an octahedron with two adatoms on the triangular faces as the most stable structure with 8 μ_B magnetic moment in 2006. Nie et al. [11] have reported that a triple tetragonal pyramid is the lowest energy structure in the triplet magnetic state in 2007. In the same year, Bhattacharyya and Majumder [12] have found a planar tetra-capped rhombus with M = 2 μ_B . In 2008, Kumar and Kawazoe [13] have stated that a bicapped octahedron converges to a hexagonal bipyramid with a magnetic moment of 2 μ_B . In 2012, Heredia et al. [15] have reported the same cubic structure of Xiao and Wang as the lowest energy configuration with 8 μ_B magnetic moment. We studied all of these reported structures and considered many other possible isomers by adding a Pt atom on the isomers of Pt₇ listed by Ge et al. [7]. Vibrational frequency calculations of all the optimized structures have also been carried out to separate stationary points from transition states.

2. Computational method

NWChem 6.0 program package [22] has been used to perform geometry optimizations and total energy calculations by spin-polarized DFT method. The generalized gradient approximation (GGA) of Becke's exchange functional [23] and Perdew et al.'s correlation functional [24] (BPW91) has been employed in the calculations. The LANL2DZ [25] and CRENBL [26] effective core potentials (ECP) and basis sets were used for Pt where the outer most 18 electrons of free Pt atom (5s²5p⁶5d⁹6s¹) are treated explicitly. The LANL2DZ and CRENBL basis sets have 22 and 40 functions of types 3s3p2d and 5s5p4d, respectively. As a first step in the investigation, more than 30 different initial configurations have been relaxed geometrically with LANL2DZ basis set and ECP for the first five spin multiplicities. Then, the chosen low-lying isomers

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have been subjected to a second geometry optimization with CRE-NBL basis set and ECP. The default convergence criteria of the program, which are 1×10^{-6} Hartree for energy, and 5×10^{-4} Hartree/ a_0 for energy gradient, were applied. The accuracy of the chosen functional together with the ECP and the basis sets was discussed on the binding energy (BE), bond length, and vibrational frequency of Pt dimer in our previous works [8].

3. Results and discussion

The structures of the obtained low-lying isomers for Pt_8 clusters are presented in Fig. 1. Binding energies per atom (BE), point group symmetries, total spin moments, HOMO–LUMO gaps, and the highest and the lowest vibrational frequencies of these structures are reported in Table 1. The isomers are listed in Table 1 from the highest to the lowest CRENBL BE. The lowest energy structure of Pt_8 clusters is identified as a triple tetragonal pyramid (TTP) which has been initiated in the geometry optimization process from a structure which is constructed by placing a Pt atom on one of the rhombic faces of the coupled tetragonal pyramid (CTP) reported by Ge and coworkers [7]. Our result is in agreement with that of Nie et al. [11] who have employed another GGA functional in their work together with a double numerical basis set augmented with polarization functions. They have calculated a BE of 3.237 eV for this structure which can be compared with our results 3.130 eV and 3.259 eV for LANL2DZ and CRENBL basis sets, respectively. The magnetic ground state is calculated as the triplet state although the singlet and the quintet states are only a few meVs above the ground state. There is another structure of Pt_8 based on the CTP configuration: trigonal face capped coupled tetragonal pyramid (TFC-CTP) which is in the quintet state.

A second group of isomers are based on the trigonal prism. FBCTP having 8 meV lower CRENBL BE than the lowest energy structure is a tilted trigonal prism with two adatoms: one is on a triangular face and the other is on a bridge side. The total magnetic

moment of this structure is $4 \mu_B$. TFCTP is a two face capped (rectangular and triangular faces are capped) CTP in the triplet state. TPCT is a distorted trigonal prism coupled with a tetrahedron in the quintet state. The back bone of the third group structures is the octahedron: OCP is an octahedron coupled with a pyramid whereas TFCO is a two face capped distorted octahedron which are in the septet and the nonet states, respectively. In the fourth group we have two bipyramidal structures: TTBP is a triple trigonal bipyramid in the septet state and DTBP-TP is double trigonal bipyramid coupled with tetragonal pyramid in the quintet state. The other three structures are edge capped double tetragonal pyramid (EC-DTP) in the triplet state, a cube in the nonet state, and an out of plane bridge capped hexagon (OPBCH) in the triplet state. To our knowledge, 7 of these structures (FBCTP, OCP, TFCTP, TPCT, TFC-CTP, DTBP-TP, EC-DTP, and OPBCH) are reported as the local minima of Pt_8 for the first time.

We have found more than one negative vibrational frequencies for the cubic structure. Hence, it is not a local minimum but a saddle point in our calculations. The other previously proposed lowest energy configurations either converge to some other isomers or have higher total energies than the isomers reported in the present study. Both of the structures given in the works of Bhattacharyya and Majumder [12] and Kumar and Kawazoe [13] have 0.11 eV (with LANL2DZ basis set) higher energies than the TTP configuration.

The number of gaussian functions in the CRENBL basis set is nearly twice of that of the LANL2DZ basis set, thus the former is more complete than the later. CRENBL BEs are higher than LANL2DZ BEs about 0.1 eV. The orders of the isomers with respect to the BEs calculated by these two basis sets and ECPs may differ. For instance, the LANL2DZ BE of the OPBCH structure is the lowest one among the listed 12 configurations, while it is the third isomer according to CRENBL BEs. Similarly, the TFCTP structure is the forth isomer with respect to LANL2DZ BEs, whereas it becomes the seventh isomer when the CRENBL basis set is employed. Although the

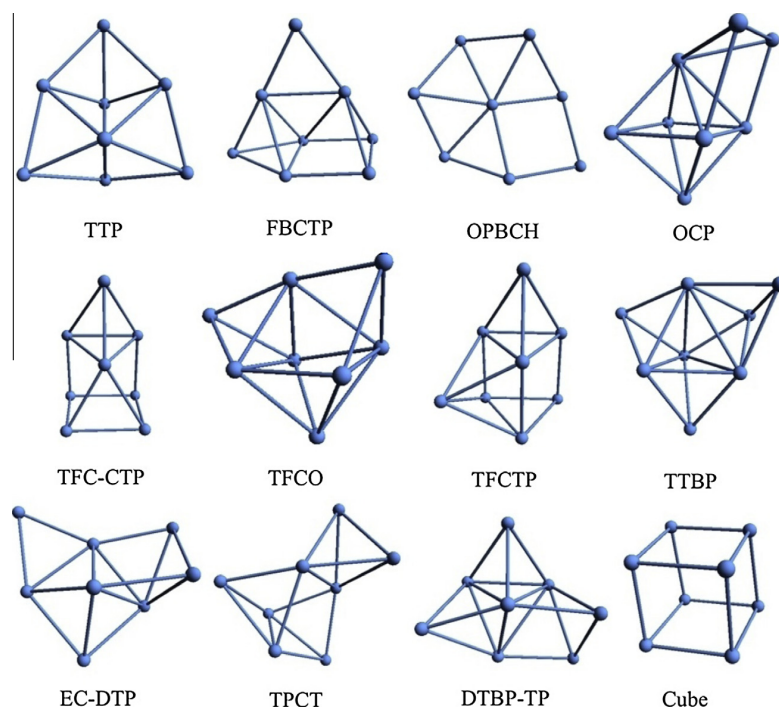


Fig. 1. Low-lying isomers of platinum octamers.

Table 1

Structures, energetics, and vibrational frequencies of the low-lying isomers of platinum octamers.

Isomeric structure	Symmetry	Spin moment (μ_B)	BE per atom (eV)		HOMO–LUMO Gap (eV) ^{ab}	ω_l and ω_h (cm ^{−1}) ^{bc}
			LANL2DZ	CRENBL		
Triple tetragonal pyramid (TTP)	C_{3v}	2	3.130	3.259	0.23	73–213
Face & bridge capped trigonal prism (FBCTP)	C_{1h}	4	3.128	3.251	0.19	74–241
Out of plane bridge capped Hexagon (OPBCH)	C_{2v}	2	3.077	3.230	0.29	20–234
Octahedron coupled pyramid (OCP)	C_{3v}	6	3.091	3.230	0.22	56–215
Trigonal face capped		4	3.084	3.226	0.20	55–229
Coupled tetragonal pyramid (TFC-CTP)	C_{3v}					
Two face capped octahedron (TFCO)	C_{1h}	8	3.085	3.218	1.50	27–204
Two face capped trigonal prism (TFCTP)	C_{3v}	2	3.090	3.213	0.31	41–216
Triple trigonal bipyramid (TTBP)	C_{3v}	6	3.087	3.213	0.21	71–217
Edge capped	C_{1h}	2	3.079	3.203	0.14	66–234
Double tetragonal pyramid (EC-DTP)						
Trigonal prism coupled tetrahedron (TPCT)	C_{2v}	4	3.088	3.203	0.22	69–236
Double trigonal bipyramid	C_{1h}	4	3.084	3.200	0.17	67–214
Coupled tetragonal pyramid (DTBP-TP)						
Cube	D_{2h}	8	3.080	3.143	1.35	–30–170 ^d

^a α -Spin^b For LANL2DZ^c Lowest and highest vibrational frequencies^d Saddle point

improvement in the basis set and ECP affects the relative stabilities of some isomers, the first two most stable structures, namely TTP and FBCTP, remain as the first and the second isomers having the highest first two BEs. 2 meV energy difference between them for the LANL2DZ basis set is enhanced to 8 meV for the CRENBL basis set.

The spin moments of the isomers changes from 2 μ_B to 8 μ_B . The two isomers with 8 μ_B spin moment (TFCO and cube) have significantly higher HOMO–LUMO gaps (more than 1 eV) than the others. All the other HOMO–LUMO gaps are between 0.14 eV and 0.31 eV. The lowest and the highest vibrational frequencies are in the range of 20–241 cm^{−1}.

4. Conclusions

In this work, we present DFT studies of the structural and electronic properties of Pt₈ cluster to locate the possible minima and ground state by performing geometry optimizations and total energy calculations in the framework of spin-polarized generalized gradient approximation. The fact that there is no consensus about the lowest energy structure of the cluster has been discussed and all the previously reported configurations together with many other possible structures have been studied. It has been found that the ground state configuration is a triple tetragonal pyramid in the triplet state. In addition, seven new local minima have been identified. HOMO–LUMO gaps and the vibrational frequencies of these minima have been reported.

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