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Highly reactive complexes with promising strong magnetic response based on gadolinium borates and oxyanions

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ABSTRACT

In this work molecular cluster calculations are performed using density functional theory to study new complexes of gadolinium borates and oxyanions. Hyperhalogen behavior is predicted for the $Gd(BO_2)_4$ cluster, which has a calculated electron affinity of 6.67 eV and a ground state spin multiplicity $2S + 1 = 7$. The results show that the GdO_2 oxyanion can be also used as building blocks of superhalogens: for $Gd(GdO_2)_4$, EA = 6.13 eV and $2S + 1 = 37$. Given that the binding energies of the BO_2 and GdO_2 dimers are comparable (1.70 and 2.49 eV, respectively), and the former can be used as building blocks of even higher reactive moieties, it is predicted that the latter can act similarly.

1. Introduction

Oxygen is the prime example among the varied types of oxidizing agents (also called oxidizers or oxidants), which are the elements or compounds that in an oxidation–reduction (redox) reaction takes electrons onto themselves from another species, i.e., they are reduced, whereas the reactants are oxidized. Explosives often consist of an inorganic oxidizing agent mixed with a reducing agent (gunpowder is such a mixture). Because the process of oxidation is so widespread used (explosives, chemical synthesis, corrosion), the term oxidizing agent has acquired multiple meanings. In the class of high energetic materials are also included the superhalogens, which consist of a central atom surrounded by halogen atoms in number that exceeds its formal valence by one [1–4]. Halogens have high electronegativity which makes them powerful oxidizing agents (in the Periodic Table, chlorine has the highest electron affinity, i.e., 3.62 eV). Superhalogens are not merely a theoretical concept, and the exceptionally high electron affinities of these species have indeed been experimentally verified [5–7]. Afterwards, new electronegative species bearing electron affinities even higher have been discovered, thus called hyperhalogens [9,10]. These consist of an atom surrounded by superhalogen moieties.

Borates are chemical compounds which contain boron oxyanions with boron in oxidation state +3. Boron most often occurs in nature as borate minerals and borosilicates. Although borates are defined by industry as any compound that contains or supplies boric oxide, these are naturally occurring minerals that exist in trace amounts in rock, soil, water and are essential for plants and animals. These are important ingredients in a variety of household and commercial products. Combined with rare earths, nickel and iron, borates can be used to make supermagnets, electromagnets for computer drives, high fidelity speakers, automobile starter motors, and various household appliances. The simplest anionic borate is the trigonal planar, BO_3^3-, which forms salts with metallic elements. BO_2 is a superhalogen with an experimental electron affinity of 4.46 eV [8]. The Au atom decorated with two BO_2 moieties has an electron affinity of 5.70 eV [10].

Gadolinium is trivalent like boron, paramagnetic at room temperature, and is widely used as an injectable contrast agent for patients undergoing magnetic resonance imaging (MRI). Gadolinium shows outstanding paramagnetic performance where a strong magnetic response is desirable. Although most gadolinium complexes are not suitable for molecular and cellular imaging, due to relatively weak unitary impact of Gd atoms on the relaxation time of hydrogen protons to provide the signal detected in MRI, ultrasmall gadolinium oxide (Gd_2O_3) nanoparticles are being developed to enhance the detectability of Gd-based contrast agents. Gadolinium oxide forms on the surface of gadolinium metal by thermal decomposition of the hydroxide, nitrate, carbonate, or oxalates. It is a highly insoluble thermally stable gadolinium source suitable for glass, optic and ceramic applications, and in high purity compositions improve both optical quality and usefulness as scientific standards. Gadolinium oxide is utilized for its high magnetic moment (7.94 μ_B) in phosphors and scintillators [11].

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Herein is reported a DFT study devoted to investigate the feasibility of obtaining new highly reactive magnetic moieties made of gadolinium borates and oxyanions. Gd being valence isoelectronic with B, GdO_2 (like BO_2) requires also one electron for shell closing. Earlier DFT calculations[12] in aluminum borates have shown that the high binding energy of the extra electron in the $Al(BO_2)_4^-$ anion is due to delocalization of the extra electron over the large number of ligand atoms, which renders large adiabatic electron affinity and high thermodynamic stability. Similarly, the delocalized character of the additional electron in the anionic cluster GdO_2^- suggests that it could be used as building blocks of superhalogens. In this sense DFT calculations are performed in this work in order to make an assessment of the structure and electronic properties of new varieties formed by assembling large sized clusters by using boron and gadolinium oxyanions as building blocks of new superhalogen moieties. From this it is expected to identify the propensity of forming new species with interesting properties such as high electron affinities and enhanced magnetic response. The uttermost reactive character of these new species and their promising strong magnetic response promote these compounds into a class of functional groups that are important in a large variety of technological applications.

2. Computational method

Calculations are performed using density functional theory with the hybrid exchange–correlation functional B3LYP [13] as implemented in the Gaussian-09 package [14]. For representing the atomic orbitals were used the SDD basis set for Gd and the 6-311+G* basis set for both B and O atoms. The former has been proved as providing reliable results for lanthanides [15], and it is actually an alternative basis set for the entire period table using effective core potentials (ECP), reducing the number of basis functions for the core electrons,besides including relativistic effects. The latter has been otherwise successfully employed in earlier DFT-B3LYP calculations in providing reliable information experimentally predicted on boron oxyanions [16]. It is worth to mention that, despite several recent papers [17–21] indicate superior functionals for calculations of electronic properties, B3LYP has been successfully employed with affordable basis set to study geometries, frequencies and electron affinities of numerous polyatomic molecule in the past years. Is is computationally less demanding than comparable conventional correlation level calculations such as second-order perturbation theory (MP2) particularly when using very large basis set. Comparative studies of the performance of hybrid density functionals for the geometry optimization of several transition-metal compounds has confirmed the reliability of B3LYP when employed with large basis. The equilibrium geometries were determined by performing multiple optimization runs, each starting from a different geometry without any constraint.

The optimized geometries thence are verified by harmonic analysis, and the nature of the stationary points is determined according to the number of negative eigenvalues of the Hessian matrix at the B3LYP level. All the vibrational frequencies were calculated using the analytic second derivative of the total energy with respect to the nuclear coordinates in order to verify the nature of the stationary point on potential energy surface. The absence of imaginary frequency modes for the optimized structure at DFT level confirms a true minimum on the potential energy surface. The optimizations of the geometries were performed using relatively tight convergence thresholds i.e., 10^{-5} hartree/bohr for the root-mean-square first derivative, with residual atomic forces no larger than 10^{-3} eV/Å.

3. Results and discussion

3.1. $(BO_2)_n$ and $(GdO_2)_n$

The ground state structures corresponding to the lowest energy configuration of neutral BO_2, $(BO_2)_2$, GdO_2, $(GdO_2)_2$ and corresponding anions are showed in Fig. 1. Note that both BO_2 and BO_2^- clusters are linear, with similar B–O bond length and same natural bond orbital (NBO) charge on the B atom. Since boron is electron donor, the extra electron in the anionic cluster goes entirely to the oxygen atoms. For the dimer $(BO_2)_2$ we see in Fig. 1 a bent form around a central O atom, which shares two equidistant B atoms. While one branch of this coordination complex has a "V" shape, the other one is linear. Particularly in this latter, the charge computed using the natural atomic orbitals (NAO) on the O atoms is about twice than that in the other ligand. The anionic GdO_2^- cluster shows a symmetrical shape built up on a planar structure centered on a rhombus with two bridged O atoms. The two diametrically opposed O atoms have shorter bond length (1.30 Å) and smaller NBO charge (-0.72e) as compared with the central pair (1.44 Å and -0.88e, respectively).

In Fig. 1 we see also the equilibrium geometries of neutral and anionic Gd-based clusters. GdO_2 has a bent shape with asymmetrical branches (bond lengths 1.84 and 2.08 Å). Gadolinium is electron donor, with NBO charge +2.08e, whereas the O atom acts as acceptor for electrons, with NBO charge -1.32 and -0.88e, respectively. In the anion we see the O atoms equidistant from Gd (bond length 1.95Å). The NBO charge on each O atom is -1.51 e, and on Gd atom it is +2.01e. With two BO_2 units attached to Gd atom we see the equilibrium geometry of the dimers $(GdO_2)_2$ and $(GdO_2)_2^-$ shown in Fig. 1. In the neutral cluster the pair of Gd atoms is connected through a triad of O atoms, each one with different NBO charge. One O atom is seen with bond length 2.17 Å and NBO charge -0.82 e. Note that none of the species has same NBO charge. On the pair of Gd atoms these are +2.28 and +2.41e, respectively. The anion $(GdO_2)_2^-$ also shows an asymmetrical shape (with different bond lengths and NBO charges) but more symmetric than in the neutral precursor, showing two bridged O atoms and two terminals O atoms.

In Table 1 are given the calculated results at the B3LYP/6-311+G (3df) level for the adiabatic electron affinity, vertical detachment energy, spin multiplicity, HOMO–LUMO gap (HLG) and binding energies. The calculated EA of BO_2 is 4.35 eV, which matches well with both recent calculations [16] and experimental results (4.46 eV) [8]. For the BO_2 dimer the calculated EA is 4.71 eV, also in agreement with earlier results. Both are superhalogens. VDE is computed as the difference in total energy of the anion and its neutral at the anion ground state geometry. For BO_2 we see in Table 1 similar values for EA and VDE, whereas for $(BO_2)_2$ VDE is 1.77 eV higher. The difference between EA and VDE gives indication of the amount of geometrical relaxation between the neutral and anionic forms. The results in Table 1 thus are consistent with the equilibrium geometries shown in Fig. 1. For GdO_2 and $(GdO_2)_2$ the calculated EA are 2.19 and 2.36 eV, respectively. Hence these are not superhalogens. In Table 1 one sees a doublet spin ground state for BO_2, while for $(BO_2)_2$ it is a singlet. For GdO_2 and $(GdO_2)_2$ we see high-spin ground states with multiplicities 9 and 17, respectively. These were determined from several calculations probing different $2S + 1$-values. Since the f-orbitals are too deep in energy and do not participate in the chemical bonding each Gd-atom contributes significantly to increase the ground state spin multiplicity. For the calculated HLG we see also in Table 1 rather significant values (the largest one for BO_2).

The binding energies of the dimers $(BO_2)_2$ and $(GdO_2)_2$ are also given in Table 1. These are comparable with those ones of Cl2