PHYSICA E
LOW-DIMENSIONAL SYSTEMS & NANOSTRUCTURES

High-spin multiplicities in ferromagnetic ground states of supramolecular halide complexes based on the gadolinium chloride
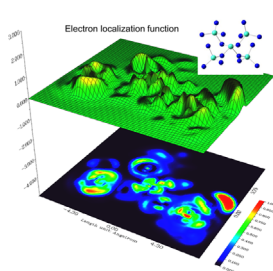
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- Supramolecular halide complexes of gadolinium are hyperhalogens.
- Strong magnetic response is predicted for the large sized clusters.
- The anion $Gd(GdCl_4)_4^-$ has $VDE = 7.70$ eV.

GRAPHICAL ABSTRACT

ABSTRACT

Calculations using density functional theory are performed to study supramolecular assemblage of high spin halide complexes based on the gadolinium chloride. With the addition of Cl atoms to both Gd and B in number that exceeds their formal valence by 1 the calculated vertical detachment energy increases to 6.08 and 5.57 eV in $GdCl_4$ and BCl_4, respectively, indicating superhalogen behavior. By using BCl_4 and $GdCl_4$ clusters as building blocks to decorate the Gd atom the vertical detachment energy increases to 7.12 and 7.70 eV in the anionic clusters $Gd(BCl_4)_4^-$ and $Gd(GdCl_4)_4^-$, respectively, which is indicative of hyperhalogen behavior. High spin multiplicities in the ferromagnetic state are observed for these clusters indicating therein outstanding paramagnetic response.

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1. Introduction

Despite its discovery in the late nineteenth century gadolinium usage however started only in more recent times. Elemental gadolinium exists in nature in the oxide minerals monazite and bastnäsite usually mingled with other rare earth metals. With an electron configuration $[Xe]4f^7 5d^1 6s^2$, few elements are as strongly magnetic as gadolinium ($\mu = 7.94\,\mu_B$), which has also the highest thermal neutron absorption cross section of any known element. The Gd^{3+} species is of special interest because of its high spin multiplicity, which is responsible for its excellence in magnetic response, essentially important in applications where measuring strong magnetic resonance is crucial. Gadolinium contrast medium contains complex carrier molecules (chelating agents) which makes certain tissues, abnormalities or disease processes more clearly visible on a magnetic resonance imaging (MRI) scans. It increases the visibility of inflammation, a tumor or growth, blood vessels, cardiac (heart) muscle scarring and assesses the blood flow to organs such as the brain and heart. Among several gadolinium compounds which are largely employed in a variety of technological applications are the gadolinium halides.

Particularly interesting is $GdCl_3$. Recent studies revealed that pre-treatment of rodents with $GdCl_3$, known as inhibitor of Kupffer cells (specialized macrophages located in the liver lining the walls of the sinusoids that form part of the reticuloendothelial system), attenuates acute liver and lung injuries, and increases the

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production of anti-inflammatory cytokines in the tissues [1–7]. For Gd, the first ionization energy is 6.15 eV [8], which is moderate (it ranges from 3.89 eV for Cs to 24.59 eV for He); its electron affinity is also modest, 0.52 eV [9]. Chlorine is otherwise the element with the highest electron affinity (*EA*) in the Periodic Table of Elements (3.62 eV), and an appreciable ionization energy (12.97 eV). Electron affinity is a measure of how much energy is released when an electron is gained by a certain atom; or, equivalently, it is also the amount of energy required in order to detach the electron from an anion. Higher electron affinity means higher reactivity, and thus it is one of the most important factors that govern the chemical reaction of atoms and molecules. Moieties with high *EAs* hence play a very important role in chemistry and are used to synthesize a wide variety of new chemical compounds.

In 1981 Gutsev and Boldyrev reported the discovery of a new class of molecules with electron affinities higher than chlorine [10], thus termed superhalogens [11–14]. These consist of a central atom surrounded by halogen atoms with a simple formula MX_{m+1}, where M is a main group or transition metal atom, X is a halogen atom, and *m* is the maximal formal valence of the metal atom M. As the number of the X atoms exceeds the maximal valence of the central atom, a substantial increase in the electron affinity of the molecule is observed. Another class of electronegative molecules with electron affinities even higher has been also reported, termed hyperhalogens [15], consisting of an atom decorated with superhalogens. The equivalent formula is MS_{m+1}, where S is the corresponding superhalogen moiety. Since highly electronegative compounds are able to accept electrons readily, their use as oxidizing agents thus opens the door for synthesizing a new class of salts adequate for an extensive variety of technological applications. Herein is investigated the structure, stability and electronic properties of highly reactive supramolecular halide clusters based on the gadolinium chloride. An assessment for assembling new superhalogen moieties from the addition of chlorine to Gd and B is made. When these are employed as building blocks decorating the Gd atom it is observed an increase of the vertical detachment energy. The results show remarkable magnetic behavior for the large sized clusters which are also strongly reactive. Considering the interesting properties of the gadolinium chloride, it is quite interesting to obtain new species bearing reactivities comparable to $GdCl_3$ or even higher, encompassed with an enhanced magnetic response associated with higher spin multiplicities, which could render a multitude of important applications for practical purposes.

2. Method

The calculations based on the density functional theory were performed with the Gaussian-09 package [16]. For the correlation density functional, the Becke 3-parameter and Lee-Yang-Parr (*B3LYP*) hybrid exchange [17] were adopted. In this study the *SDD* basis for Gd and the 6-311+G(3df) set for B and Cl are adopted. Scalar relativistic effects in gadolinium have been accounted for using the quasi-relativistic 28-electron effective core potential (*MWB28 ECP*) [18]. The reliability of *SDD* has been well proven for lanthanides [19]. Actually it is an alternative basis set for the entire periodic table using effective core potentials (pseudopotentials), reducing the number of basis functions for the core electrons, and which includes relativistic effects. The equilibrium geometries were obtained by performing multiple optimization runs, each starting from a different geometry of the complex, without any constraint in the potential energy surface. The optimized geometries are then characterized by harmonic vibrational frequency 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. 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) and the residual atomic forces no larger than 10^{-3} eV /Å. Natural bond orbital analysis was performed with the NBO 5.0 code [20].

3. Results and discussion

3.1. $GdCl_n$

The 4f electrons are located too deep in energy to participate in chemical bonding, and our calculations in several clusters indeed confirm that the highest oxidation state of Gd with respect to Cl is +3. In Fig. 1 are shown the equilibrium geometries of neutral and anionic clusters assembled by means of successive attachments of Cl atoms to Gd (bond lengths and charges obtained using the natural population analysis (NPA) are indicated). Cl is an acceptor for electrons whereas Gd is a donor. With one Cl atom bonded to Gd the calculated Gd–Cl bond length in the neutral cluster is 2.49 Å, while same NBO charge (0.82 e) is seen in both species. In the anion, the Gd–Cl bond length increases to 2.66 Å, and the extra electron is mostly found in Cl. With two Cl atoms attached to Gd, both neutral and anionic clusters bear a "V" shape. In $GdCl_2$ the NBO charges on Gd and Cl are +1.62 e and −0.81 e, respectively, and the Gd–Cl bond length is 2.53 Å. In the anion the additional electron goes almost entirely to partially neutralize the charge on Gd, thereby decreasing the NBO charge to +0.75 e. The ionic Gd–Cl bond increases to 2.63 Å. The addition of three Cl atoms to Gd forms the $GdCl_3$ cluster, which has a pyramidal shape (C_{3v} symmetry), with Gd–Cl bond lengths of 2.49 Å; the NBO charge is +2.22 e on Gd and −0.74 e on Cl. The anion otherwise has planar structure with trigonal shape (C_{3h} symmetry), with longer Gd–Cl bond lengths (2.63 Å). The NBO charge on Gd and Cl are +1.60 e and −0.87 e, respectively. The addition of a fourth Cl atom to Gd leads to the larger cluster $GdCl_4$, where it exceeded the formal valence of Gd (+3). The neutral cluster has C_{2v} symmetry. The Cl atoms are seen arranged in pairs with Gd–Cl bond lengths 2.49 and 2.68 Å, and NBO charge −0.73 and −0.39 e; Gd shows the largest donation of electrons (+2.25 e). The anion $GdCl_4^-$ has tetrahedral shape (T_d symmetry), where the Gd–Cl bond length is 2.57 Å.

In Fig. 2 are displayed the fragmentation energies calculated for two different decay channels, namely, Cl and Cl_2, which gives an estimation of the relative thermodynamic stabilities of $GdCl_n$. In Fig. 2 histogram plots of the calculated electron affinity (*EA*), given by the difference in the total energies of the anion and neutral ground states, which gives a measure of the energy gain due to the addition of an extra electron is also shown. The dissociative energies are thus computed as $\delta E_{ne} = E(GdCl_n) - E(GdCl_{n-p}) - E(Cl_p)$, $n = 1 \rightarrow 4$ and $p = 1,2$, for both Cl and Cl_2 decomposition channels of the neutral clusters, and likewise for the anionic clusters. From Fig. 2 it can be seen how these clusters, both neutral and anions, would likely prefer to dissociate through the decay channel corresponding to the yield of Cl. The decay channel of lowest energy of $GdCl_4$ is ascribed to dissociation into $GdCl_2 + Cl_2$. The low fragmentation energy shows that this cluster is of the van der Waals type. The electron affinity increases throughout the series until reaching 5.82 eV in $GdCl_4$, far exceeding that one of chlorine (indicated in Fig. 2 by the dotted line). $GdCl_4$ is a superhalogen.

The calculated results for the vertical detachment energy (*VDE*), total magnetic moment and the difference Δ_{HL} between highest occupied molecular orbital (*HOMO*) and lowest unoccupied