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Electronic structure and molecular properties of paramagnetic hexanuclear Tantalum $[Ta_6X_{12}Y_6]^{3-}$ (X and Y = F, Cl, Br, I) cluster compounds

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ABSTRACT

Relativistic density functional calculations were carried out on several Tantalum cluster of the general formula $[Ta_6X_{12}Y_6]^{3-}$, with the aim to characterize and analyze their molecular structure and electronic properties, in order to gain more insights into their stability and reactivity. Herein are reported the geometrical parameters, electronic structures, excitation energies and magnetic properties, of a series of clusters that have been and have not been yet synthesized. The calculated Δg tensor shows that as the halide capping ligand become heavier the Δg tensor values increases due to spin–orbit effects. Through the use of the reactivity indexes it is shown that when the axial ligand is iodine it becomes the most reactive and labile ligand. The TD-DFT calculations on the complete $[Ta_6X_{12}Y_6]^{3-}$ cluster family show good agreement with the available experimental data.

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1. Introduction

The study of edge-bridged octahedral cluster dominates the chemistry of Tantalum metal since their first characterizations in solution in the 50's [1] and since then represents an important class of compounds in cluster chemistry [2,3]. Hexanuclear cluster compounds of the early transition metals with halide ligands adopt two common structural motifs, those constituted by the group VI metals $[M_6X_8Y_6]^{2-}$ (M = Mo and W) and those constituted by the group V metals $[M_6X_{12}Y_6]^{n-}$ (M = Nb and Ta) [3–8]. In both structures each metallic atom has one available site for the attachment of a terminal ligand. This terminal ligand could be of different nature, like halogens, –CN, –SCN, carbon chains, etc. [6–8].

Negative [8–10], neutral [11] and positive [12–14] charged complexes have been prepared with the $[Ta_6X_{12}]^{n+}$ central core with different oxidation states (X = Br and Cl; n = 1–5), and all these clusters show interesting catalytic properties and reactivity patterns [14–18]. All the paramagnetic clusters with general formula $[Ta_6X_{12}Y_6]^{3-}$, are chemically and thermodynamically stable under a variety of conditions and its molecular structure are constituted of an octahedral arrays of metal atoms, 12 edge capping halide ligands (labeled X) and six outer (axial) ligands (labeled Y). The Y ligands are terminally bonded one to each metal center as shown in Fig. 1. The X or capping ligand are inert in front of the substitutions, while the axial or Y ligands are more labile, as was shown by Prokopuk et al. [19]. In these sense the $[Ta_6X_{12}Y_6]^{3-}$ cluster, undergo easy and reversible reduction and oxidation to $[Ta_6X_{12}Y_6]^{2-}$ and $[Ta_6X_{12}Y_6]^{4-}$, respectively. Due to this oxidation–reduction behavior these clusters represent an interesting class of metal catalyzer clusters [14–18]. The electron donor strength of the axial ligand influences the substitutional lability of these sites and also the stability of the oxidation states of these clusters. For instance, phosphine ligands, which are π acceptors, stabilize the lower oxidation states and the π donor halogen ligand stabilizes the higher oxidation states. [20–22]. Thus, the study of metallic cluster involves the knowledge of the electronic structure, stability, reactivity, spectroscopic, structural and photophysical properties [23,24].

Previously, Ogliaro et al. [25] carried out several DFT calculations reporting only the scalar relativistic corrections on a family of complexes with general formula $[M_6X_{12}Y_6]^{n-}$ (where M = Nb and Ta, X = two bonded inner capping halide ligand and Y = two electron donor axial ligand). This study allowed a better understanding of the stability of the compounds and it also established a relationship between their structural arrangement and the number of electrons available for metal–metal bonding in M_6 clusters. Recently, Ramirez-Tagle and Arratia-Pérez [26] reported the influence of the axial substituents over the composition of the frontier molecular orbitals for this kind of complexes, and it was also observed that energy changes in their frontier orbitals affected the reactivity. For these reasons it is important to evaluate the electronic structure and molecular properties of these paramagnetic clusters. In terms of the possible Jahn–Teller distortion, we argue that due to the SO effect these clusters cannot distort because of a Kramer degeneracy in their ground state.

Nevertheless, despite the numerous experimental and theoretical studies devoted to these compounds, no systematic detailed

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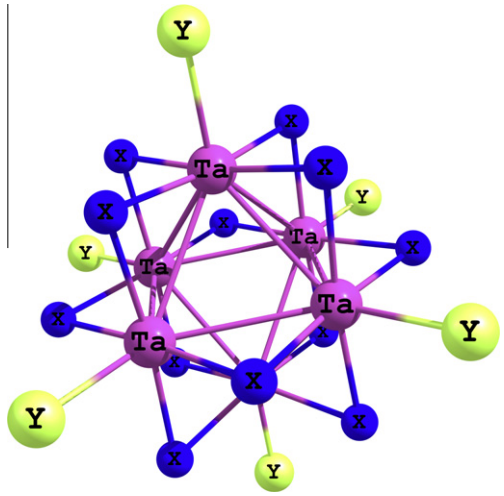

Fig. 1. Diagram of the cluster $[Ta_6X_{12}Y_6]^{3-}$.

analysis has been done. With the aim to get more knowledge in the previous mentioned topics in this work we report the frontier molecular orbital analysis, reactivity indexes, a simulation of the UV–Vis absorption spectra of 16 $[Ta6X_{12}Y_6]^{3-}$ clusters (where X = F, Cl, Br and I; Y = F, Cl, Br and I) and its paramagnetic EPR parameters. Of all of these 16 clusters only the $[Ta_6Cl_{12}Y_6]^{3-}$ with Y = Cl, Br and I, were previously reported [19,27].

2. Computational details

All geometries and properties of $[Ta_6X_{12}Y_6]^{3-}$ clusters were calculated employing the ADF2008.01 code [28]. The calculations were carried out using the zeroth order regular approximation (ZORA) Hamiltonian including scalar and spin–orbit (SO) relativistic corrections [29,30] and the triple-ζ slater basis set plus two polarization functions (STO-TZ2P) [31,32].

The molecular structures were fully optimized with constrained O_h symmetry via generalized gradient approximation (GGA) method with non-local exchange and correlation corrections within the BP86 functional proposed by Becke and Perdew [33,34], using unrestricted open-shell calculations. The excitation energies were estimated using time dependent density functional theory (TD-DFT) including relativistic scalar effects [35–37] and the LB94 model (Van Leeuwen and Baerends) which is specially designed for the calculation of optical properties [38]. Solvation effects were modeled by "Conductor-like Screening Model" (COSMO) for real solvents [39,40] using acetonitrile as solvent. The EPR calculations were performed using the BP86 functional, for the calculation of *g* isotropic values, the spin–orbit ZORA relativistic restricted open shell approach has been used [41–43].

3. Results and discussion

The newest X-ray structure of $[Ta_6Cl_{12}Cl_6]^{3-}$ was reported in 2004 [27] and the absorption spectra of the $[Ta_6Cl_{12}Y_6]^{3-}$ (with Y = Cl, Br, I) family was reported by Prokopuk et al. [19]. Due to both previously reported data we carried out the prediction of the geometrical parameters, electronic structures, excitation energies and magnetic properties, of a series of clusters that have not been yet synthesized, *vide infra*. Also a proposition of their applications as catalyzers is made.

3.1. Molecular structure

The results of the geometry optimization with scalar relativistic and with the SO approximation were performed using acetonitrile as solvent. The intramolecular distances of the O_h clusters are reported in Table 1. A general cluster molecular structure is depicted in Fig. 1. All the calculated bond distances are in good agreement with the experimental values for the cluster that have crystallographic report, see Table 1 [27]. This indicates that both approximations (scalar and SO) are efficient to determinate geometrical parameters of this kind of heavy metal clusters. This fact was previously reported by Ramirez-Tagle and Arratia-Pérez [26]. Besides our calculations are in good agreement with the previously calculated geometries at the LDA/DZP level [25]. A comparison of all the herein reported cluster subfamilies was carried on (see Table 1). Looking at only one type of axial ligand (labeled as Y) and changing the capping halide ligand (labeled as X) all the distances turn larger as the capping ligand turns heavier. In this sense, in the group that contains $[Ta_6F_{12}]^{3+}$ as central core, the Ta–Ta and Ta–F distances are 2.83 and 2.12 Å, respectively. The same distances in the subfamily that contains $[Ta_6I_{12}]^{3+}$ as central core are 3.04 and 2.90 Å, respectively. As could be observed a slight enlargement of both distances is observed as the halide capping atom turn heavier. Furthermore, the bond distance between the metal atom and the axial halide ligand increases as the capping ligand turns heavier. This situation can be more clearly observed when the axial ligand is iodine, see Table 1.

Otherwise, if the central core $[Ta_6X_{12}]^{3+}$ is fixed (without changing the capping ligand) and the axial halide atom is changed, the distance between the axial halide and the Ta metal atom increases, while all the other distances remain the same.

Table 1
Selected bond distances (Å) for all the complexes with scalar (sc.) and spin–orbit (SO) relativistic corrections.

		$[Ta_6F_{12}Y_6]^{3-}$		$[Ta_6Cl_{12}Y_6]^{3-}$		Exp.*	LDA**	$[Ta_6Br_{12}Y_6]^{3-}$		LDA**	$[Ta_6I_{12}F_6]^{3-}$	
		sc.	SO	sc.	SO			sc.	SO		sc.	SO
Y = F	Ta–Ta	2.83	2.84	2.96	2.97			2.99	3.01		3.03	3.05
	Ta–F/Cl/Br/I	2.14	2.14	2.52	2.52			2.68	2.68		2.90	2.90
	Ta–F	2.08	2.07	2.09	2.08			2.09	2.09		2.10	2.10
Y = Cl	Ta–Ta	2.83	2.84	2.97	2.99	2.93	2.95	3.01	3.03	2.99	3.04	3.06
	Ta–F/Cl/Br/I	2.13	2.13	2.50	2.50	2.44	2.57	2.65	2.66	2.66	2.85	2.85
	Ta–Cl	2.52	2.52	2.60	2.59	2.57	2.6	2.64	2.63	2.8	2.74	2.73
Y = Br	Ta–Ta	2.83	2.84	2.97	2.98			3.00	3.02		3.04	3.06
	Ta–F/Cl/Br/I	2.12	2.13	2.49	2.49			2.65	2.65		2.85	2.85
	Ta–Br	2.69	2.69	2.79	2.78			2.85	2.84		2.98	2.97
Y = I	Ta–Ta	2.83	2.85	2.97	2.98			3.00	3.02		3.03	3.05
	Ta–F/Cl/Br/I	2.12	2.13	2.49	2.49			2.64	2.65		2.84	2.85
	Ta–I	2.91	2.91	3.02	3.02			3.09	3.08		3.25	3.24

* [19].
** [25].

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