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Electronic Structure of Diamagnetic and Paramagnetic Hexanuclear Chalcohalide Clusters of Rhenium

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Hexanuclear chalcohalide clusters of rhenium(III) of general formula $[Re_6S_{4+x}Cl_{10-x}]^{x-}$ with $x = 1$–4 have been studied using quantum chemical DFT calculations. The optimized structures reproduce the geometrical features found from X-ray data for the members of the series. The relative stability of different stereoisomers for the mono- and dianions has been estimated. The analysis of the tetraanion series $[Re_6Q_8X_6]^{4-}$ with Q = S, Se and X = Cl, Br, I, and CN demonstrates the influence of the μ_1- and μ_3-ligands on the strength of Re–apical ligand bond. It is shown that the tetragonal distortion found for the stable oxidized paramagnetic species $[Re_6S_8Cl_6]^{\bullet 3-}$ results from the Jahn–Teller effect for a doubly degenerate electronic state.

I. Introduction

Hexanuclear chalcohalide clusters of rhenium(III) have attracted much attention in recent years.[1,2] The synthesis of $Re_6S_4Cl_{10}$ by Fedorov[3] in 1971 and, 10 years later, the work of Leduc et al.[4] laid the foundation of an extensive high-temperature solid-state chemistry of hexanuclear rhenium chalcohalide clusters. Their octahedral cores, $[Re_6(\mu_3\text{-Y})_{4+x}(\mu_3\text{-X})_{4-x}]^{(6-x)+}$ (X halogen, Y chalcogen, $n = 0-4$), are isostructural to the molybdenum chalcogenide analogues, in the superconducting Chevrel−Sergent phases.[5] The inner core can be prepared only by high-temperature solid-state reactions. The development of a molecular chemistry of their soluble cluster forms started in 1987, with the discovery of the solubility of $KRe_6Se_5Cl_9$ in ethanol.[6] The molecular clusters constitute a series of anions formed by an octahedron of rhenium(III) (Figure 1), included in a cube of eight chalcogen and/or halogen μ_3-ligands, noted “inner” by Schäfer and von Schnering.[7] The coordination of the rhenium atoms is completed by six halogen μ_1-ligands in an apical position. Changing the chalcogen/halogen ratio, the total charge of the anions could be varied from −1 to −4, without noticeable influence on their shape or volume. Now, the preparation of salts, either with mineral (Li, K, Na, Rb, Cs, Zn, Ca) or with organic (ammonium or phosphonium) cations is known for $[Re_6S_5Cl_9]^-$,[8a] for $[Re_6S_6Cl_8]^{2-}$,[8a,b] for $[Re_6S_7Cl_7]^{3-}$,[8c] and for $[Re_6S_8Cl_6]^{4-}$.[8d] These clusters provide a rare set of isosteric anions which allow us to modulate the properties of hybrid inorganic−organic molecular materials. The charge of the anions defines the filling of the electronic bands whereas their structure is governed by the packing of organic radical cations. The inorganic anions can contribute to the

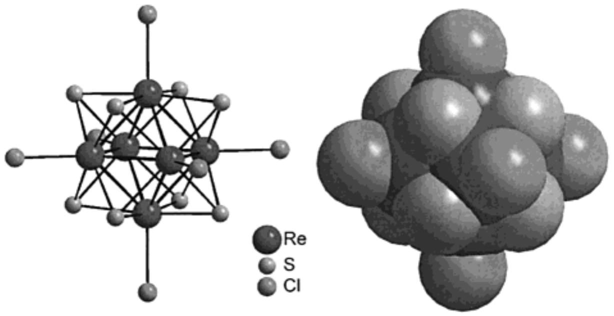

Figure 1. Ball-and-stick and ball representations of the octahedral rhenium cluster $[Re_6S_8Cl_6]^{4-}$: All sulfur atoms are “inner” ligands and all apical positions are occupied by chlorine atoms.

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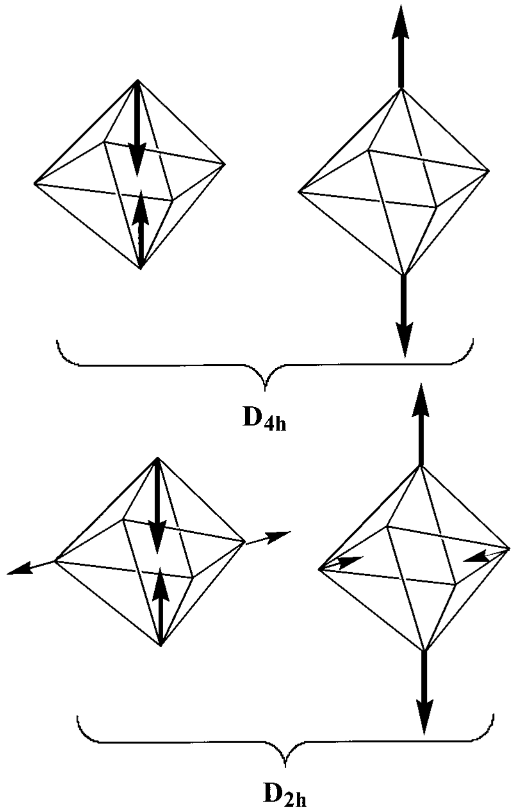

Figure 2. Schematical representation of the D_{4h} and D_{2h} distortions of the rhenium octahedral cores.

magnetic or optical properties of solids. The tetraanionic cluster, $[Re_6S_8Cl_6]^{4-}$, occupies a special place in the series. It is distinguished by its solubility, optical properties, chemical reactivity, and, especially, for its ability to be easily oxidized. The corresponding paramagnetic cluster, $[Re_6S_8Cl_6]^{\bullet 3-}$, can be isolated and has been found to be luminescent.[9] This cluster exhibits a distortion from octahedral symmetry, which has not been found in other clusters of such type. EPR and X-ray diffraction data have shown that, between 100 and 200 K, a distortion of the oxidized species, $[Re_6S_8Cl_6]^{\bullet 3-}$, occurs in which the cluster is compressed along the C_4 axis (Figure 2).[10] It has been found recently that the similar and isoelectronic cluster $[Re_6S_8(CN)_6]^{\bullet 3-}$ also presents a distortion from the octahedral geometry even at room temperature, but in this case, the cluster is elongated along the C_4 axis.[11]

Although several papers dealing with the qualitative description of the electronic structure of the hexanuclear rhenium clusters can be found in the literature, there is no comparative quantum chemical study of the compounds of this family. We present here the calculations on the mono-, di-, tri-, and tetraanions $[Re_6S_{4+x}Cl_{10-x}]^{x-}$ with $x = 1-4$. In the series of mono- and dianions, three stereoisomers can exist. We show that, in both cases, one stereoisomer is favored, and in the case of the dianion, this result agrees with the experimental observations. The effects of μ_1- or μ_3-ligand substitution on the geometry and the reactivity of the tetraanionic clusters $[Re_6Q_8X_6]^{4-}$ with Q = S, Se and X = Cl, Br, I, and CN are also analyzed. Finally, the distortion of the oxidized species is studied by calculations in different symmetry groups and attributed to the Jahn–Teller effect.

II. Theoretical Details

All the calculations were carried out with the ADF program[12] version 2000.02 using a triple-ζ plus polarization Slater basis set to describe the valence electrons of all atoms except rhenium atoms. We have used a frozen core composed of 1s states for C and N, of 1s–2p for S and Cl, and of 1s–3p states for Se and Br. For iodine atoms, a frozen core composed of 1s–4p states was used, but no polarization function has been added. For rhenium atoms, a frozen core composed of the 1s–4f states was used, and 5s, 5p, 5d, 6s, and 6p states were described by a triple-ζ Slater basis. The relativistic corrections for the Re atoms are very important to yield a correct prediction of equilibrium structures. They were introduced by the ZORA (zero order regular approximation) method.[13] The geometries and the energies were calculated using gradient corrections. The local spin density approximation characterized by the electron gas exchange together with the Vosko–Wilk–Nusair parametrization[14] for correlation was used. Becke's nonlocal corrections[15] to the exchange energy and Perdew's nonlocal corrections[16] to the correlation energy were added. The geometry optimizations of the clusters were performed under the constraints of an appropriate point symmetry group. Spin-unrestricted calculations were used for the open-shell configurations.

III. Results and Discussion

(a) Electronic Structure of the Tetraanionic Diamagnetic Species: $[Re_6Q_8X_6]^{4-}$ with Q = S, Se and X = Cl, Br, I, CN. The calculations for the tetraanionic cluster $[Re_6S_8Cl_6]^{4-}$ have been performed in the O_h symmetry group. All attempts to lower the symmetry converged again to the same O_h geometry. The structural parameters obtained as a result of optimization (Table 1) are in good agreement with the structural data. The rhenium–rhenium distances are well reproduced, and the rhenium–ligand distances are slightly longer than the experimental ones (the difference does not

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Table 1. Distances in $[Re_6Q_8X_6]^{4-}$ Clusters with Q = S, Se and X = Cl, Br, I, CN Obtained by Geometry Optimizations and Structural Data of the Cluster at Room Temperature

distances[a] in Å	opposite Re−Re	adjacent Re−Re	Re−Q bond	Re−X bond
$[Re_6S_8Cl_6]^{4-}$ [b] mean	3.684 ⟨3.681⟩	2.605 ⟨2.601⟩	2.436 ⟨2.404⟩	2.486 ⟨2.451⟩
$[Re_6S_8Br_6]^{4-}$ [c] mean	3.681 ⟨3.668⟩	2.603 ⟨2.594⟩	2.437 ⟨2.396	2.623 ⟨2.595⟩
$[Re_6S_8I_6]^{4-}$ [d] mean	3.682 ⟨3.676⟩	2.604 ⟨2.599⟩	2.445 ⟨2.40⟩	2.825 ⟨2.786⟩
$[Re_6S_8CN_6]^{4-}$ [e] mean	3.653 ⟨3.680⟩	2.583 ⟨2.602⟩	2.431 ⟨2.413⟩	2.092 (Re−C) ⟨2.122⟩
$[Re_6Se_8Cl_6]^{4-}$ [f] mean	3.718 ⟨3.697⟩	2.629 ⟨2.614⟩	2.542 ⟨2.523⟩	2.505 ⟨2.431⟩
$[Re_6Se_8CN_6]^{4-}$ [g] mean	3.688 ⟨3.724⟩	2.607 ⟨2.634⟩	2.525 ⟨2.52⟩	2.082 (Re−C) ⟨2.10⟩

[a] As the symmetry group of the salts is $P\bar{1}$, the distances given in the cluster are averaged, although no significant distortion of the clusters is observed. [b] $[nNBu_4]_4[Re_6S_8Cl_6]$.[8d] [c] $[nNBu_4]_4[Re_6S_8Br_6]$.[8d] [d] $[nNBu_4]_4[Re_6S_8I_6]$.[8d] [e] $NaCs_3[Re_6S_8(CN)_6]$.[17] [f] $Tl_4[Re_6Se_8Cl_6],TlCl$.[8d] [g] $NaCs_3[Re_6Se_8(CN)_6]$.[17]

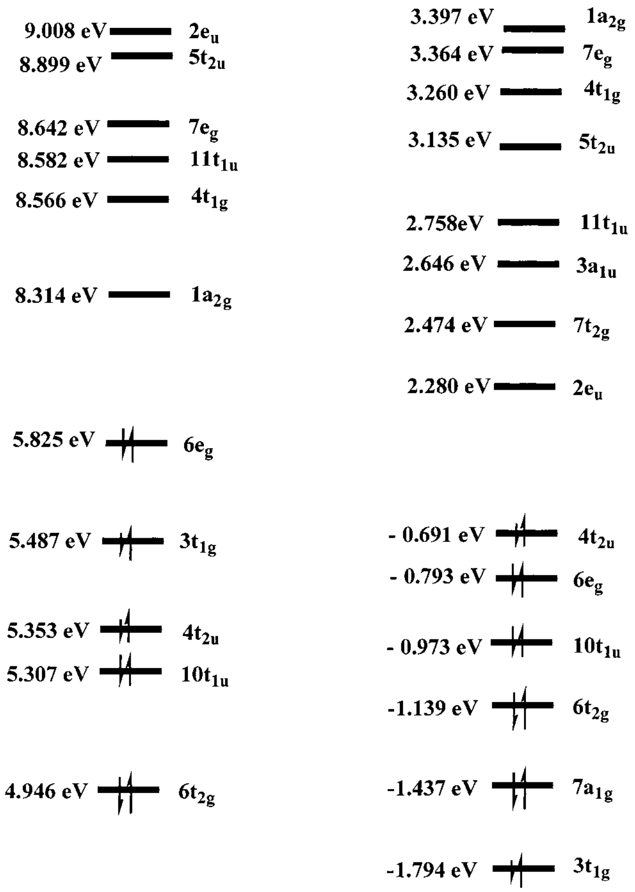

Figure 3. Electronic levels scheme for the tetraanionic cluster $[Re_6S_8Cl_6]^{4-}$ and its analogue tungsten cluster $[W_6Cl_{14}]^{2-}$.

exceed 1.5%). The experimental data show that the structure of the rhenium core remains unchanged for all closed shell clusters. At the same time, it has been reported that the Re−Cl distances strongly depend on the nature of the countercation in the salt.[8b,9] This shows that the rhenium−apical ligand bonds are very sensitive to the effects of environment. Our calculations in the gas phase do not take into account the crystal effects.

The energy levels diagram is shown in Figure 3. The important feature of the electronic structure is the doubly degenerate HOMO (labeled $6e_g$), well separated (2.4 eV) from the LUMO. In consequence, a Jahn−Teller effect can be expected in oxidized species. The important gap is responsible for the absence of a pseudo-Jahn−Teller effect, hence explaining that no symmetry lowering is found. The frontier orbitals are mostly centered on the metal atoms (in particular, the two HOMOs and the two LUMOs). The composition of the HOMO differs from that given by Arriata-Perrez et al.[18] In their results, the main contribution into the HOMO is provided by the orbitals of apical ligands. The experimental data show that the lowest energy absorption band of the cluster in solution depends on the nature of ligands.[8d,9] It means that a molecular orbital other than HOMO, HOMO − 1 and LUMO, LUMO + 1 must be implicated into the lowest energy electronic transition. This limitation is also imposed by the selection rules, which do not allow dipole transitions between these states. Regarding the nature and the symmetry of the orbitals, the electronic structure of $[Re_6S_8Cl_6]^{4-}$ is very similar to the one calculated for the isoelectronic tungsten cluster $[W_6Cl_{14}]^{2-}$. However, the order of the orbitals is slightly changed. The main difference comes from the inversion between HOMO and HOMO − 2, resulting in the degenerate t_{2u} HOMO. This inversion is probably due to the electronegativity difference between tungsten and rhenium from one part, and between sulfur and chlorine μ_3-ligands from another part. We must note that e_g HOMO for $[W_6Cl_{14}]^{2-}$ was proposed by Gray et al. on the basis of a qualitative model of energy levels,[19] which did not include explicitly ligand orbitals.

The substitution of all chlorine μ_1-ligands by another halide or cyanide ligand and/or the substitution of all sulfur μ_3-ligands by selenium ligands preserves the charge carried by the anions and does not modify the cluster symmetry (point group O_h). A comparison of the geometry and the electronic structure among the series is thus possible to explore a subtle change of reactivity in the series of these clusters. The results of the geometry optimization are given in Table 1. The geometry of the rhenium octahedron core appears independent of the nature of the apical ligands. However, it is modified when sulfur is substituted by selenium. The increase in Re−Re distances can be explained by the larger size of selenium atoms.[20] In agreement with the experimental data, the substitution of halide has no effect on the geometry of the cluster core. The Re−X bond length increases in the series Cl, Br, I, as expected. The case of cyanide ligands appears singular among the series. The substitution of apical ligands by cyanide affects slightly the geometry of the

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Table 2. Atomic Mulliken Charges in the Clusters $[Re_6Q_8X_6]^{4-}$ with Q = S, Se and X = Cl, Br, I, CN

atomic charge	Re	Q	X
$[Re_6S_8Cl_6]^{4-}$	+0.288	−0.276	−0.586
$[Re_6S_8Br_6]^{4-}$	+0.287	−0.235	−0.640
$[Re_6S_8I_6]^{4-}$	+0.023	−0.147	−0.493
$[Re_6S_8CN_6]^{4-}$	+0.172	−0.220	−0.156 (C), −0.389 (N)
$[Re_6Se_8Cl_6]^{4-}$	+0.475	−0.413	−0.591
$[Re_6Se_8CN_6]^{4-}$	+0.327	−0.338	−0.131 (C), −0.412 (N)

rhenium core by a shortening of the Re−Re distances. The rhenium−chalcogenide bonds are not affected, suggesting that the change in the central octahedron is essentially due to the modification of the chemical nature of the Re−CN bond, by back-donation of the rhenium atoms to the cyanide groups. However, these subtle shortenings (less than 1%) have not been observed until now in the structural data for the cyanide cluster salts.

A Mulliken analysis of the charge carried by the atoms among the series (Table 2) can give some preliminary data about the ability of different atoms in the clusters to participate in hydrogen bonds formed in molecular materials. The most negative charge is carried by the apical ligands. The role of the Cl atoms as acceptors of hydrogen bonds can be anticipated by the observation of the structural arrangement of the inorganic−organic hybrid materials.[21]

The absence of polarization functions for the iodine atoms in the ADF program does not allow us to directly compare the overlap population values to estimate the relative strength of Re bonds with apical ligands. Therefore, we performed calculations with the same basis set of atomic orbitals (double-ζ without polarization orbital) at equilibrium geometry. The overlap population in the bond decreases with atomic mass (from 0.082 for $[Re_6S_8Cl_6]^{4-}$ to 0.043 for $[Re_6S_8Br_6]^{4-}$ and 0.005 for $[Re_6S_8I_6]^{4-}$). It shows that the rhenium−chlorine bond is stronger than the rhenium−bromine bond or rhenium−iodine bond. The weakening of the Re−halogen bond is also found when sulfur is substituted by selenium (from 0.082 for $[Re_6S_8Cl_6]^{4-}$ to 0.07 for $[Re_6Se_8Cl_6]^{4-}$). In fact, the cluster with the weakest Re−halogen bond $[Re_6Se_8I_6]^{4-}$ is usually used as starting material to obtain substituted selenium clusters, by simple action of silver salts or smooth heating.[22]

(b) Mono-, Di-, and Trianionic Species: $[Re_6S_5Cl_9]^{1-}$, $[Re_6S_6Cl_8]^{2-}$, and $[Re_6S_7Cl_7]^{3-}$. Contrary to tetraanions, the mono-, di- and trianionic species $[Re_6S_{4+x}Cl_{10-x}]^{x-}$ ($x = 1-3$) do not obey the O_h symmetry group. The symmetry group of the trianion is C_{3v}. Depending on the distribution of chloride ligands on the inner cube of the cluster, three stereoisomers can exist for the monoanions: two with C_s-symmetry, named *fac* and *mer*, and one, *diag*, with C_{3v}-symmetry as shown in Figure 4a. For dianions, also three stereoisomers are possible: *fac* and *syn* with C_{2v}-symmetry, and *diag* with D_{3d}-symmetry (Figure 4b).

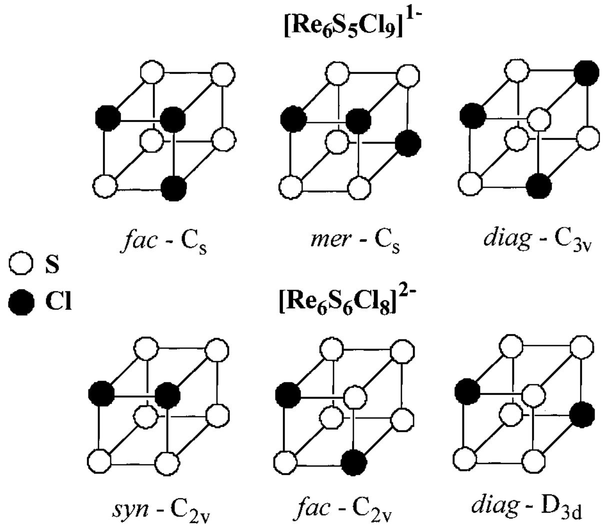

Figure 4. Distribution of the chloride ligands in the cube of the inner ligands and the energy of the three stereoisomers for the monoanionic $[Re_6S_5Cl_9]^{1-}$ and the dianionic $[Re_6S_6Cl_8]^{2-}$ clusters.

Our calculations show that in the case of the monoanions the two *fac* and *mer* isomers have very close energies (differing by less than 0.001 eV) and are much more stable (by 0.535 eV) than the *diag* isomer. Unfortunately, the available structural data (see, for example, ref 23) do not allow us to distinguish the positions of Cl and S for the monoanion. For the dianion, the only observed isomer in the solid state is the centrosymmetric one (*diag*).[21,24] Our calculations are in agreement with this observation: the *diag* isomer is the most stable, and the *fac* isomer has the highest energy. We can note that there is no simple relation between the Cl−Cl distance in the inner cube and the energies of the different isomers.

On the basis of extended Hückel calculations, Canadell et al.[20] proposed that, in the series of rhenium clusters, the rhenium−apical chlorine distance depends on the total charge of the anion. The increase of the charge of the cluster results in pushing away the negatively charged chloride ligands. The same interpretation was proposed for the change of the Mo−Cl distances in the series $[Mo_6(Se_nCl_{8-n})Cl_6]^{(2+n)-}$ ($n = 0-2$) by Ebihara et al.[25] Our DFT calculations confirm this result (Table 3). In particular, all the stereoisomers for the monoanion and the dianion possess the same apical Re−Cl bonds. Thus, this rhenium−chlorine distance is not dependent on the symmetry of inner cube but on the total charge carried by the anion.

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Table 3. Symmetry and Re−Cl$_a$ Distances in Clusters $[Re_6S_{4+x}Cl_{10-x}]^{x-}$ with $x = 1-4$

cluster	point group	Re−Cl$_a$ distance^a Å
$[Re_6S_8Cl_6]^{4-}$	O_h	2.486
$[Re_6S_7Cl_7]^{3-}$	C_{3v}	⟨2.433⟩
$[Re_6S_6Cl_8]^{2-}$ *trans*	D_{3d}	2.389
$[Re_6S_6Cl_8]^{2-}$ *fac*	C_{2v}	⟨2.389⟩
$[Re_6S_6Cl_8]^{2-}$ *syn*	C_{2v}	⟨2.388⟩
$[Re_6S_5Cl_9]^{1-}$ *diag*	C_{3v}	⟨2.350⟩
$[Re_6S_5Cl_9]^{1-}$ *fac*	C_s	⟨2.352⟩
$[Re_6S_5Cl_9]^{1-}$ *mer*	C_s	⟨2.352⟩

^{a} When the distances are not equivalent, an average is given.

(c) Distortions and Jahn−Teller Effect in the Open Shell Species: $[Re_6S_8Cl_6]^{•3-}$. The calculations of the oxidized $[Re_6S_8Cl_6]^{•3-}$ cluster in the O_h point symmetry group led to a partly filled e_g HOMO. This result suggests the possibility of the Jahn−Teller effect in the oxidized species. As we did not want to privilege a priori a particular type of Jahn−Teller distortion, we studied all possibilities existing for an E-term octahedral system. As it is stated by the general theory of the Jahn−Teller effect,[26] the adiabatic surface of an E-term octahedral system can possess either of the following three types of minima: (a) three equivalent minima corresponding to the elongation to D_{4h} symmetry (noted D_{4h}^{el}); (b) three equivalent minima corresponding to the compression to D_{4h} symmetry (noted D_{4h}^{com}); and (c) six equivalent minima corresponding to the distortion to D_{2h} symmetry. All three possibilities were explored by imposing a particular initial distortion in the geometry optimization. In all cases, a stabilization relative to the high-symmetry O_h structure was found. Surprisingly, in all three cases, our calculations converged to minima of different energy which are ordered as $E(D_{4h}^{com}) < E(D_{4h}^{el}) < E(D_{2h})$. The minima of lowest energy correspond to tetragonally compressed octahedra. We can note that this type of distortion was observed experimentally in $(n\mathrm{Bu}_4\mathrm{N})_3[Re_6S_8Cl_6]$ at 100 K.[10] The possibility of achieving the convergence of DFT calculations in different contradicting geometries is due to the monodeterminant nature of DFT methods. The stabilization of the distorted structure can be achieved through the stabilization of each orbital (in our case, these are the 13 a_{1g} and 6 b_{1g} orbitals of the D_{4h} group) belonging to the degenerate manifold in highly symmetrical geometry. This effect was illustrated by Daul et al. in their DFT calculations of the VCl_4 complex.[27] The difference between the energy of the cluster in O_h and D_{4h} symmetry allows us to estimate the Jahn−Teller stabilization energy[26,28] which is of the order of 0.06 eV. The second-order Jahn−Teller coupling, which is responsible for the wrapping of the Mexican hat adiabatic surface, can be estimated from the difference between two D_{4h} configurations. This energy is found to be about 0.005 eV.

It is instructive to consider the influence of the oxidation and resulting Jahn−Teller distortions on the metal−metal bonding in clusters. The Re−Re overlap populations go from 3.2365 to 3.0891 and 3.6462 in the oxidized cluster. For each Re atom, two metal−metal bonds become stronger, and two other bonds, weaker than in the parent cluster.

In the distorted structure, mainly the distances between opposite Re and S atoms are affected. The change of the former ones is as large as 0.1 Å. However, the average distances in the inner part of the cluster remain unchanged, and its volume is not modified by oxidation. The Re−Cl average distance (⟨2.433⟩ Å for $[Re_6S_8Cl_6]^{•3-}$) decreases and becomes exactly equal to the value found for $[Re_6S_7Cl_7]^{3-}$. This result agrees with the sensitivity of the Re−Cl bonds to the total charge of the cluster.

One could suspect that the additional stabilization of the oxidized anion $[Re_6S_8Cl_6]^{•3-}$ due to the Jahn−Teller effect contributes to the weak value of the redox potential of the couple $[Re_6S_8Cl_6]^{4-}/[Re_6S_8Cl_6]^{•3-}$.

A Jahn−Teller distortion could also be expected for the $[W_6Cl_{14}]^{•1-}$ cluster with the degenerate noncompletely filled t_{2u} HOMO. Indeed, a tetragonal distortion has been proposed for the interpretation of the EPR data in frozen solution.[29] The Jahn−Teller effect in a cubic system, characterized by a triply degenerate T-term, can result in distortions either along E_g, or along T_{2g}, normal coordinate.[26] Our calculations of the oxidized $[W_6Cl_{14}]^{•1-}$ cluster resulted in a local minimum corresponding to the symmetry of the D_{4h} group. However, the energy of the D_{4h} minimum was found to be 0.016 eV higher than the energy of the structure optimized under the constraints of the O_h symmetry group. To avoid this contradiction, we, following the procedure proposed by Daul,[27] recalculated the energy of the O_h structure occupying selectively the components of the degenerate t_{2u} orbitals. This new calculation led to a stabilization of the tetragonally distorted structure by 0.001 eV compared to the high-symmetry case. This value gives a measure of the Jahn−Teller stabilization energy for the tungsten complex. We must note that the similar calculations for the rhenium complex practicaly do not modify the value of the Jahn−Teller energy given previously. One can conclude that the Jahn−Teller effect is much weaker for the tungsten cluster. This difference results from the contrasting nature of the HOMOs for the two clusters. In fact, as it was indicated by Lin and Williams,[30] the t_{2u} orbitals significantly mix with the antibonding combinations derived from the d(π) basis sets. The more pronounced bonding nature of the e_g orbital confers upon it a larger influence over the molecular shape. A symmetry lowering due to the Jahn−Teller could also be expected for oxidized derivatives of some mono-, di-, and trianions of the rhenium cluster, because some of them possess a degenerate HOMO. This point would need further theoretical study.

IV. Conclusions

The hexanuclear chalcohalide rhenium clusters are important components of hybrid inorganic−organic materials

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with interesting optical, chemical, and magnetic properties. The understanding of the electronic structure of these clusters is a main prerequisite for the crystal engineering of new materials with original properties. In our calculations, we considered all members of the family of clusters and showed that the structural variations can be rationalized on the basis of simple considerations. The geometry of the rhenium core remains quasi-unchanged along the series. The bond strength with more reactive apical ligands is modulated by the total charge of the anion and the nature of μ_3-ligands. More negative charges found for apical ligands make them the best eventual acceptors of weak hydrogen bonds, which are mainly of electrostatic nature.[31] To perform a quantitative analysis of the ability to form hydrogen bonds, calculations taking into account environmental effects are needed.

One important aspect concerns the Jahn−Teller origin of the structural distortions in the oxidized anion $[Re_6S_8Cl_6]^{\bullet 3-}$. It is the first example of the Jahn−Teller effect in the series. It is well-known that the Jahn−Teller effect often leads to very particular spectroscopic properties of molecular and solid-state systems. Further theoretical and experimental studies are needed to elucidate the role of the Jahn−Teller effect in the physical properties of materials containing the $[Re_6S_8Cl_6]^{\bullet 3-}$ cluster.

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