First-principles study of the hexahalogenotechnetate(IV) ions TcX$_6^{2-}$ [X = Cl, Br]

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**Abstract**

We report all-electron scalar relativistic calculations of the structural and electronic properties of the octahedral hexahalogenotechnetate(IV) ions TcX$_6^{2-}$ [X = Cl, Br] using spin-polarized density functional theory. The calculated bond distances are in good agreement with X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) data available for salts of hexachloride and hexabromide technetate ions. Molecular-orbital analysis shows the importance of the hybridization between Tc 4d orbitals and p orbitals of the ligands. Normal modes of vibration of the hexachloride and hexabromide complexes of Tc and Re have also been computed and assessed by comparison with spectral data for salt crystals of technetate/rhenenate complex ions.

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1. Introduction

Alkali metal chloride-based melts are actively considered as possible reaction media for pyrochemical processing of spent nuclear fuels containing the long-lived $^{99}$Tc ($^{99}Tc$ ($t_{1/2}$ = 2.13 $\times$ 10$^5$ years, $\beta^-$ = 294 keV) [1]. The reduction reaction of rhenium and technetium oxides with hydrochloric acid in alkali metal molten salts leads to the production of the hexachloro ions ReCl$_6^{2-}$ and TcCl$_6^{2-}$, respectively. Understanding the coordination and electronic structure of halogenotechnetate complexes is of paramount importance in the development of novel pyrochemical processes for treating spent nuclear fuels.

Hexachloride and hexabromide complexes of Re(IV) and Tc(IV) in various cubic host crystals have received extensive experimental attention over the last few decades [1–6]. This is in stark contrast with the scarcity of theoretical studies reported so far on these complexes. In particular, computational studies of the hexahalogenotechnetate(IV) ions TcX$_6^{2-}$ [X = Cl, Br] have been limited to the simplified orbital valence force field (OVFF) and Urey–Bradley force field (UBFF) calculations carried out by Mehta [7] and the X$_s$–SW muffin–tin calculations by Hartmann et al. [8].

In this Letter, we report all-electron scalar relativistic calculations of the total energies, optimized geometries, and electronic properties of octahedral halogen-complex ions TcX$_6^{2-}$ [X = Cl, Br] using spin-polarized density functional theory (DFT). To the best of our knowledge, this study is a first step assessment of the accuracy of all-electron relativistic first-principles calculations in modeling hexahalogenotechnetate(IV) complex ions. This DFT approach is expected to provide a more accurate and detailed understanding of the metal-ligand bonding in these complexes compared to previous force-field studies. Theoretical analysis of the type and strength of bonding at the molecular level should shed light on the electronic structure and stability of these systems. A detailed vibrational mode analysis for hexachloride and hexabromide complexes of Re(IV) and Tc(IV) is also reported in this study and assessed by comparison with spectral data for potassium and cesium salts of hexachloride and hexabromide technetate/rhenenate ions.

2. Computational methods

First-principles all-electron scalar relativistic calculations of the total energies and optimized geometries were performed using the spin-polarized density functional theory [9]. It is commonly observed that inclusion of relativistic effects decreases the computed lengths of bonds involving heavy atoms and improves spectroscopic properties compared to similar non-relativistic calculations [10]. The exchange correlation energy was calculated using the local gradient approximation (LDA) with the parametrization of Perdew and Wang (PWC) [11]. Double numerical basis sets including polarization functions on all atoms (DNP) were used in the calculations. The DNP basis set corresponds to a double-$\zeta$ quality basis set with $d$-type polarization functions added to atoms heavier than hydrogen. The DNP basis set is comparable to 6–31G$^*$ Gaussian basis sets [12] with a better accuracy for a similar basis set size [9]. In the generation of the numerical basis sets, a global orbital cutoff of 4.8 Å was used. The energy tolerance in the self-consistent field calculations was set to 10$^{-6}$ Hartree. Optimized geometries were obtained using the direct inversion in a subspace method (DIIS) with an energy convergence tolerance of 10$^{-5}$ Hartree and a gradient convergence of 2 $\times$ 10$^{-3}$ Hartree/Å. Structural optimizations...
and electronic properties calculations were performed at the Γ point. This computational approach has shown previously to yield accurate structural results for Tc-bearing complexes and compounds [13–15].

3. Results and discussion

The optimized geometries of the TcX2- [X = Cl, Br] ions are found to have octahedral symmetry (O₆ point-group symmetry; cf. Fig. 1). The calculated Tc–Cl bond distance is 2.366 Å, in excellent agreement with the experimental values of 2.35 and 2.37 Å reported previously from single crystal X-ray diffraction (XRD) [2] and extended X-ray absorption fine structure (EXAFS) [4] studies of K₂TcCl₆, respectively. The computed Tc–Br bond distance of 2.526 Å also reproduces the distance of 2.52 Å determined from both XRD and EXAFS measurements [4]. These values are close to the sum of the effective ionic radii of Tc and X with formal charges +4 and −1, respectively: r_{Tc} + r_{Cl} = 2.45 Å and r_{Tc} + r_{Br} = 2.61 Å [16].

Using the Hirshfeld partitioning of the electron density, the partial charge carried by the Tc atom is found to vary from +0.110e in TcCl₂ to +0.054e in TcBr₂, with charges of −0.351e and −0.342e on Cl and Br, respectively. The electronic charge transferred from Tc to the surrounding halogen atoms decreases slightly from Cl to Br, consistent with the decrease of the electronegativity and the increase of the atomic radius down the halogen series. For the sake of comparison, the bond distances calculated at the same level of theory for the ReCl₂ and ReBr₂ ions with O₆ symmetry are d(Re–Cl) = 2.360 Å and d(Re–Br) = 2.521 Å, and the partial charge carried by the Re atom varies from +0.185e in ReCl₂ to +0.134e in ReBr₂, with charges of −0.364e and −0.356e on Cl and Br, respectively. The computed Re–Cl bond distance is in close agreement with the 2.37 Å value reported experimentally [17].

Energy level diagrams for the TcX₂⁻ [X = Cl, Br] ions with octahedral symmetry, computed using spin-unrestricted DFT, are displayed in Fig. 2, along with the corresponding representation of the molecular orbitals (MOs) near the HOMO–LUMO gap of TcBr₂ in Fig. 3. The molecular orbitals of TcCl₂ have not been represented as they show only minute differences with the ones of TcBr₂. From group theoretical considerations, it is shown that d-orbitals in an ion placed at the center of an octahedral field of ligands split into two sets of orbitals, i.e. dₓz and dₓ₋zᵧ orbitals, and dᵧz, dₓz and dₓz, each of these orbitals being energetically degenerate within these two sets. Referring to the character table of the O₆ group, the dₓz and dₓ₋zᵧ wavefunctions and the dᵧz, dₓz, and dₓz, wavefunctions form a basis set for the respective Eₓ and Tₓz representations of the group [18]. Therefore, eₓ electrons and tₓz electrons of Tc occupy the dₓz and dₓ₋zᵧ orbitals and the dᵧz, dₓz, and dₓz, orbitals, respectively. The eₓ orbitals are higher-lying in energy than the tₓz orbitals, as a result of electrostatic repulsive forces between the d electron and the negatively charged ligands and the fact that the electronic charge is much more concentrated along the ion-ligand directions in the dₓz₋zᵧ (eₓ) orbital than in the dᵧz (tₓz) orbital (cf. Fig. 3). The computed energy differences, Δₓz, between the 2eₓ and 2tₓz molecular states resulting from the Tc d electron surrounded by an octahedral array of Cl and Br ligands are 2.53 and 2.19 eV, respectively. These values of energy splitting...
of the metal d-orbitals are typical of weak-field ligands such as Br and Cl. In addition, the value of the splitting $\Delta p$ produced by Br ligands appears slightly smaller than the one for Cl ligands, consistent with the empirically-derived spectrochemical series [19].

A standard indicator of kinetic stability and chemical hardness of molecular systems is given by the energy separation between the highest occupied molecular orbital (HOMO, $\pi$-spin $2t_{2g}$) and the lowest occupied molecular orbital (LUMO, $\pi^*$-spin $2t_{2g}$), a large energy gap implies high stability [20,21]. The calculated HOMO–LUMO gaps are comparable for TcCl$_6^-$ ($\Delta E = 1.19$ eV) and TcBr$_6^-$ ($\Delta E = 1.12$ eV). This, in addition to the larger value of $\Delta p$ for TcCl$_6^-$ compared to TcBr$_6^-$, tends to suggest that TcCl$_6^-$ is slightly more stable than TcBr$_6^-$. As shown in Fig. 3, the $2e_g$ and $2t_{2g}$ non-bonding molecular orbitals of the TcX$_6^-$ [X = Cl, Br] complexes both include Tc $4p$ and X $p$ atomic contributions. The lower-lying MOs $1t_{1g}$, $2t_{1u}$, and $1f_{2u}$, only exhibit $p$ character from the halide ligands. In the $1t_{1g}$ MO, some degree of $pp\sigma$ bonding appears between the halide ligands, while some small non-bonding Tc $4p$ is also observed. The $1f_{2u}$ MO is composed of Tc $d_{xy}$ orbitals forming three $p$ bonds with the $p$ orbitals of the ligands which are shared equally among the six Tc–X pairs. The $1e_g$ MO is characterized by strong $\sigma$ bonding between the metal $d_{z^2}$ orbital and the $p$ orbitals of the ligands. Finally, the $1a_1g$ MO is a $\sigma$ bonding orbital resulting from $s-p$ hybridization between Tc and the halide ligands.

Normal modes of vibration of MX$_6^-$ [M = Tc, Re; X = Cl, Br] complexes both include Tc $4d$ and X $p$ atomic contributions. The lower-lying MOs $1t_{1g}$, $2t_{1u}$, and $1f_{2u}$ only exhibit $p$ character from the halide ligands. In the $1t_{1g}$ MO, some degree of $pp\sigma$ bonding appears between the halide ligands, while some small non-bonding Tc $4p$ is also observed. The $1f_{2u}$ MO is composed of Tc $d_{xy}$ orbitals forming three $p$ bonds with the $p$ orbitals of the ligands which are shared equally among the six Tc–X pairs. The $1e_g$ MO is characterized by strong $\sigma$ bonding between the metal $d_{z^2}$ orbital and the $p$ orbitals of the ligands. Finally, the $1a_1g$ MO is a $\sigma$ bonding orbital resulting from $s-p$ hybridization between Tc and the halide ligands.

Table 1

<table>
<thead>
<tr>
<th>MX$_6^-$</th>
<th>Frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TcCl$_6^-$</td>
<td>v(1) = 293, v(2) = 243, v(3) = 101, v(4) = 87, v(5) = 57</td>
</tr>
<tr>
<td>K$_2$[TcCl$_6$]</td>
<td>Exp. 208, 176, 243, 123, 115</td>
</tr>
<tr>
<td>Cs$_2$[TcCl$_6$]</td>
<td>Exp. 204, 176, 242, 119, 112</td>
</tr>
<tr>
<td>TcBr$_6^-$</td>
<td>DFT 314, 255, 322, 158, 143, 99</td>
</tr>
<tr>
<td>K$_2$[TcBr$_6$]</td>
<td>Exp. 342, 270, 321, 185, 177</td>
</tr>
<tr>
<td>Cs$_2$[TcBr$_6$]</td>
<td>Exp. 335, 265, 309, 181, 177</td>
</tr>
<tr>
<td>ReCl$_6^-$</td>
<td>DFT 201, 164, 215, 100, 89, 62</td>
</tr>
<tr>
<td>K$_2$[ReCl$_6$]</td>
<td>Exp. 218, 170, 221, 125, 117</td>
</tr>
<tr>
<td>Cs$_2$[ReCl$_6$]</td>
<td>Exp. 214, 170, 217, 123, 115</td>
</tr>
<tr>
<td>ReBr$_6^-$</td>
<td>DFT 328, 274, 303, 152, 143, 105</td>
</tr>
<tr>
<td>K$_2$[ReBr$_6$]</td>
<td>Exp. 346, 274, 321, 177, 176</td>
</tr>
<tr>
<td>Cs$_2$[ReBr$_6$]</td>
<td>Exp. 342, 271, 309, 174, 175</td>
</tr>
</tbody>
</table>

Fig. 4. Frequencies (in cm$^{-1}$) of the normal modes of vibration of the MX$_6^-$ complexes [M = Tc, Re; X = Cl, Br]. Results of density functional calculations are reported in the left column and the experimental values assigned by Schwochau and Krasser [22] for potassium and cesium salts of MX$_6^-$ are displayed in the middle and right columns, respectively.

101 cm$^{-1}$, respectively, for TcBr$_6^-$ and 158 cm$^{-1}$ and 322 cm$^{-1}$ for TcCl$_6^-$.

The calculated frequencies of the three Raman-active modes, i.e. $v_1(\tau_{2u})$, $v_2(\varepsilon_g)$ and $v_3(\tau_{2g})$, are 192, 152 and 87 cm$^{-1}$ for TcBr$_6^-$ and 314, 255 and 143 cm$^{-1}$ for TcCl$_6^-$. The lowest frequency, $v_4(\tau_{2u})$, corresponds to an inactive vibrational mode in both IR and Raman experiments. Due to the weak intermolecular forces existing at ambient conditions in molecular solids, the structural identity of TcBr$_6^-$ and TcCl$_6^-$ complexes is expected to be essentially preserved in the condensed state [23,24]. Indeed, the computed frequencies of isolated MX$_6^-$ complexes are comparable with the frequencies observed by Schwochau and Krasser [22] in the vibrational spectra of potassium and cesium salts of hexachloride and hexabromide technetate/rhenate ions (cf. Table 1 and Fig. 4). The best agreement is reached for the highest frequency, $v_1(\tau_{2u})$, while lower frequencies measured in salt crystals tend to be blueshifted compared to frequencies calculated for the free MX$_6^-$ complexes. Such frequency shifts from gas phase values are expected for molecules in a confined environment [25].

In summary, all-electron scalar relativistic DFT calculations of the octahedral of hexahalogenotechnetate(IV) ions TcX$_6^-$ [X = Cl, Br] are found to successfully reproduce structural properties of salts of hexachloride and hexabromide technetate ions determined from XRD and EXAFS experiments. Molecular-orbital analysis shows the importance of the hybridization between Tc 4d orbitals and p orbitals of the ligands. Computed normal modes of vibration of the hexachloride and hexabromide complexes of Tc and Re are in fair agreement with spectral data for salt crystals of technetate/rhenate complex ions. Further computational effort will investigate the influence of the salt crystal host on the structural.
Acknowledgments

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References