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/rhenate 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 β^--emitting technetium isotope, ^{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_α–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/rhenate 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-ζ 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 2×10^{-3} Hartree/Å. Structural optimizations

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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 TcX_6^{2-} [X = Cl, Br] ions are found to have octahedral symmetry (O_h 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 K_2TcCl_6, 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: $r_{Tc} + r_{Cl} = 2.45$ 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 $TcCl_6^{2-}$ to $+0.054e$ in $TcBr_6^{2-}$, 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 $ReCl_6^{2-}$ and $ReBr_6^{2-}$ ions with O_h symmetry are $d(Re - Cl) = 2.360$ and $d(Re - Br) = 2.521$ Å, and the partial charge carried by the Re atom varies from $+0.185e$ in $ReCl_6^{2-}$ to $+0.134e$ in $ReBr_6^{2-}$, 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 TcX_6^{2-} [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 $TcBr_6^{2-}$ in Fig. 3. The molecular orbitals of $TcCl_6^{2-}$ have not been represented as they show only minute differences with the ones of $TcBr_6^{2-}$. 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. d_{z^2} and $d_{x^2-y^2}$ orbitals, and d_{xy}, d_{xz} and d_{yz} orbitals, each of these orbitals being energetically degenerate within these two sets. Referring to the character table of the O_h group, the d_{z^2} and $d_{x^2-y^2}$ wavefunctions and the d_{xy}, d_{xz} and d_{yz} wavefunctions form a basis set for the respective E_g and T_{2g} representations of the group [18]. Therefore, e_g electrons and t_{2g} electrons of Tc occupy the d_{z^2} and $d_{x^2-y^2}$ orbitals and the d_{xy},
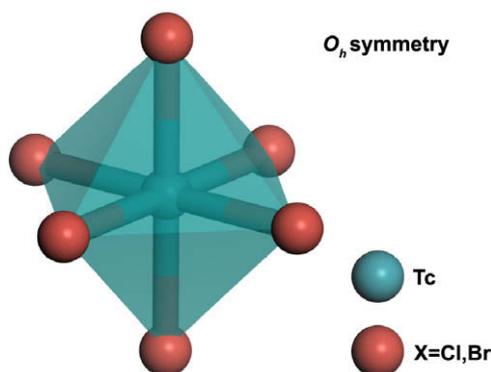
Fig. 2. Molecular-orbital energy level diagrams for the TcX_6^{2-} [X = Cl, Br] complexes with O_h symmetry calculated using all-electron scalar relativistic spin-polarized density functional theory.

Fig. 3. Molecular orbitals near the HOMO–LUMO gap of $TcBr_6^{2-}$ (O_h symmetry) calculated using all-electron scalar relativistic spin-polarized density functional theory.

Fig. 1. Schematic representation of the TcX_6^{2-} [X = Cl, Br] complexes calculated using all-electron scalar relativistic spin-polarized density functional theory. The Tc atom is located at the center of a regular coordination octahedron.
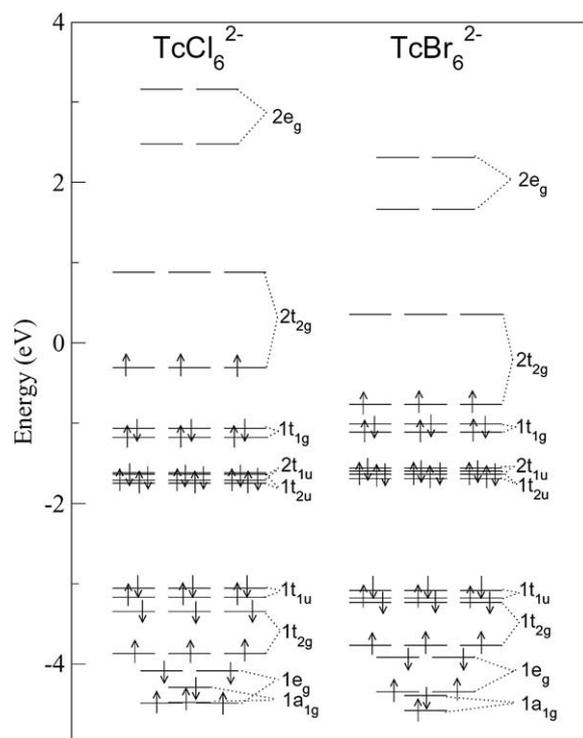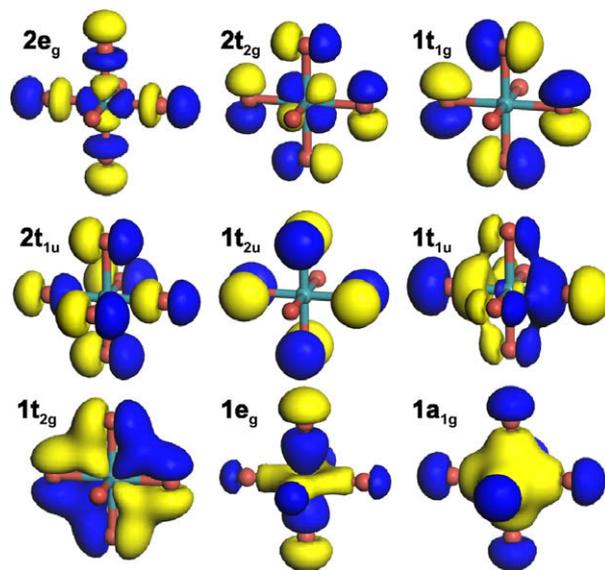
d_{xz} and d_{yz} orbitals, respectively. The e_g orbitals are higher-lying in energy than the t_{2g} orbitals, as a result of electrostatic repulsive forces between the d electron and the negatively charged ligands and the fact that the electronic charge is much more concentrated along the ion-ligand directions in the $d_{x^2-y^2}$ (e_g) orbital than in the d_{xy} (t_{2g}) orbital (cf. Fig. 3). The computed energy differences, Δ_0, between the $2e_g$ and $2t_{2g}$ molecular states resulting from the Tc d electron surrounded by an octahedral array of Cl and Br ligands are 2.55 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 Δ_0 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, α-spin $2t_{2g}$) and the lowest occupied molecular orbital (LUMO, β-spin $2t_{2g}$), a large energy gap implies high stability [20,21]. The calculated HOMO–LUMO gaps are comparable for $TcCl_6^{2-}$ ($\Delta E = 1.19$ eV) and $TcBr_6^{2-}$ ($\Delta E = 1.12$ eV). This, in addition to the larger value of Δ_0 for $TcCl_6^{2-}$ compared to $TcBr_6^{2-}$, tends to suggest that $TcCl_6^{2-}$ is slightly more stable than $TcBr_6^{2-}$.

As shown in Fig. 3, the $2e_g$ and $2t_{2g}$ non-bonding molecular orbitals of the TcX_6^{2-} [X = Cl, Br] complexes both include Tc $4d$ and X p atomic contributions. The lower-lying MOs $1t_{1g}$, $2t_{1u}$, and $1t_{2u}$, only exhibit p character from the halide ligands. In the $1t_{1u}$ MO, some degree of $pp\sigma$ bonding appears between the halide ligands, while some small non-bonding Tc $4p$ is also observed. The $1t_{2g}$ MO is composed of Tc d_{xy} orbitals forming three π 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 σ bonding between the metal $d_{x^2-y^2}$ orbital and the p orbitals of the ligands. Finally, the $1a_{1g}$ MO is a σ bonding orbital resulting from $s - p$ hybridization between Tc and the halide ligands.

Normal modes of vibration of MX_6^{2-} [M = Tc, Re; X = Cl, Br] with O_h symmetry have also been calculated using finite differences of the analytic gradient of energy with respect to atomic positions (cf. Table 1 and Fig. 4). All atoms were used to evaluate Hessian matrix elements. As nonlinear molecules with seven atoms $TcBr_6^{2-}$ and $TcCl_6^{2-}$ have $3(7) - 6 = 15$ degrees of internal freedom. The representation Γ of these molecules with O_h symmetry reduces as follows: $\Gamma = A_{1g} + E_g + T_{1g} + 3T_{1u} + T_{2g} + T_{2u}$. Examination of the character table shows that the rotations and translations belong to the T_{1g} and T_{1u} representations. Discarding rotational and translational modes, we obtain the following list of genuine normal modes, grouped according to the activities of their fundamentals: $2T_{1u}$, infrared-active; A_{1g}, E_g, T_{2g}, Raman-active; T_{2u}, inactive. The representations generated by the set of six Tc–X bonds, Γ_{TcX}, and the set of twelve XTcX angles, Γ_{XTcX}, can be reduced as follows: $\Gamma_{TcX} = A_{1g} + E_g + T_{1u}$ and $\Gamma_{XTcX} = T_{1u} + T_{2g} + T_{2u}$. The two T_{1u} modes each involve a combination of bond stretching and angle deformation, the A_{1g} and E_g genuine modes involve only bond stretching, while the T_{2g} and T_{2u} modes correspond only to angle deformation. The computed frequencies of the two IR-active modes, i.e. $v_3(\tau_{1u})$ and $v_4(\tau_{1u})$, are 243 and

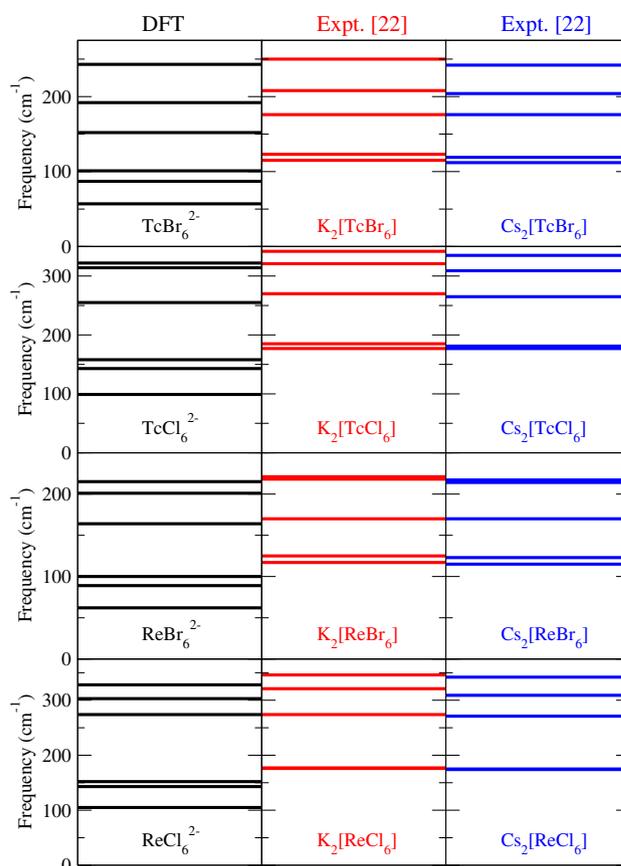**Fig. 4.** Frequencies (in cm^{-1}) of the normal modes of vibration of the MX_6^{2-} complexes [M = Tc, Re; X = Cl, Br]. Results of density functional calculations are reported in the left column and the experimental values assigned by Schwochau and Krasser [22] for potassium and cesium salts of MX_6^{2-} are displayed in the middle and right columns, respectively.

101 cm^{-1}, respectively, for $TcBr_6^{2-}$ and 158 cm^{-1} and 322 cm^{-1} for $TcCl_6^{2-}$. The calculated frequencies of the three Raman-active modes, i.e. $v_1(\alpha_{1g})$, $v_2(\epsilon_g)$ and $v_5(\tau_{2g})$, are 192, 152 and 87 cm^{-1} for $TcBr_6^{2-}$ and 314, 255 and 143 cm^{-1} for $TcCl_6^{2-}$. The lowest frequency, $v_6(\tau_{2u})$, 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 spectral and structural identity of $TcBr_6^{2-}$ and $TcCl_6^{2-}$ complexes is expected to be essentially preserved in the condensed state [23,24]. Indeed, the computed frequencies of isolated MX_6^{2-} 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, $v_3(\tau_{1u})$, while lower frequencies measured in salt crystals tend to be blueshifted compared to frequencies calculated for the free MX_6^{2-} 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^{2-} [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,

Table 1
Calculated and observed frequencies (in cm^{-1}) of the normal modes of vibration of the MX_6^{2-} complexes [M=Tc, Re; X = Cl, Br]. Experimental values assigned by Schwochau and Krasser [22] correspond to potassium and cesium salts of MX_6^{2-}.

MX_6^{2-}		Frequencies					
		$v_1(\alpha_{1g})$	$v_2(\epsilon_g)$	$v_3(\tau_{1u})$	$v_4(\tau_{1u})$	$v_5(\tau_{2g})$	$v_6(\tau_{2u})$
$TcBr_6^{2-}$	DFT	192	152	243	101	87	57
$K_2[TcBr_6]$	Exp.	208	176	250	123	115	–
$Cs_2[TcBr_6]$	Exp.	204	176	242	119	112	–
$TcCl_6^{2-}$	DFT	314	255	322	158	143	99
$K_2[TcCl_6]$	Exp.	342	270	321	185	177	–
$Cs_2[TcCl_6]$	Exp.	335	265	309	181	177	–
$ReBr_6^{2-}$	DFT	201	164	215	100	89	62
$K_2[ReBr_6]$	Exp.	218	170	221	125	117	–
$Cs_2[ReBr_6]$	Exp.	214	170	217	123	115	–
$ReCl_6^{2-}$	DFT	328	274	303	152	143	105
$K_2[ReCl_6]$	Exp.	346	274	321	177	176	–
$Cs_2[ReCl_6]$	Exp.	342	271	309	174	175	–

electronic, and vibrational properties of hexahalogenotechnetate(IV) ions.

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