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High-Valent Technetium Fluorides. Does TcF_7 Exist?

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The structures and stabilities of technetium fluorides in high oxidation states have been studied quantum-chemically at density functional theory (B3LYP) and coupled-cluster (CCSD(T)) levels. The calculations indicate clearly that technetium heptafluoride, TcF_7, has a good chance of existence and preparation, thus providing the first heptafluoride in the 4d series. The $[TcF_6]^+$ cation, a potential precursor, is also computed to be thermochemically stable against gas-phase elimination reactions. The problem with such highly fluorinated complexes appears thus to be mainly in difficult synthetic access under typical condensed-phase conditions. Matrix-isolation techniques or gas-phase experiments appear to be better suited as starting points.

1. Introduction

The high oxidation state +VII is only known for a small range of transition-metal complexes (see Table 1 for oxides, fluorides, and oxyfluorides). In particular, the only homoleptic fluoride complexes with this oxidation number confirmed unequivocally by experiment are $[ReF_8]^-$ and ReF_7. The latter is thus also the only well-established heptafluoride of the transition metals.[1] The isolation of OsF_7, reported in 1966,[2] could recently not be reproduced under the indicated conditions[3] (reaction of metal powder with F_2 at 620 °C and 400 bar with subsequent rapid cooling) and is therefore subject to doubt (our recent quantum chemical study indicates OsF_7 nevertheless to be a viable target for preparation under matrix or gas-phase conditions[4]). High-level quantum-chemical calculations have predicted furthermore the existence of IrF_7, representing an extension of iridium oxidation states to +VII, but experimental confirmation is as yet not available.[5] Finally, AuF_7, claimed to have been prepared in the 1980s,[6,7] was shown by calculations to probably have been the complex $AuF_5 \cdot F_2$[8,9] and thus does not represent oxidation state +VII.

Table 1. Summary of Experimentally Established, Experimentally Misassigned (in Parentheses), and Computationally Predicted (in Italics) Transition-Metal Oxide, Oxyfluoride, and Fluoride Complexes with Oxidation State +VII[a]

element	oxide	oxyfluoride	fluoride
Mn	$[MnO_4]^{-\ 47}$ $Mn_2O_7{}^{47}$	MnO_3F^{48}	
Tc	$[TcO_4]^{-\ 49}$ $Tc_2O_7{}^{50}$	$TcO_3F^{13,51-53}$ $TcO_2F_3{}^{54-56}$ $TcOF_5{}^{42}$	*TcF_7*
Ru	$[RuO_4]^{-\ 47}$		s
Re	$Re_2O_7{}^{57}$	ReO_3F^{58} $ReO_2F_3{}^{58}$ $ReOF_5{}^{59}$	$ReF_7{}^{1,60}$ $ReF_8{}^{-\ 61}$
Os	$[OsO_4]^{-\ 62}$ M_5OsO_6 (M = Li, Na)[63]	$(OsO_3F)^{64\ b}$ $(OsO_2F_3)^{65,66\ b}$ $OsOF_5{}^{65,67-70}$	*$OsF_7{}^{2\ c}$*
Ir			*$IrF_7{}^{5}$*
Au			$(AuF_7)^d$

[a] Only oxide, oxyfluoride, and fluoride complexes are shown. [b] The previously reported oxyfluorides OsO_3F and OsO_2F_3 have been found not to be true Os(VII) species.[3] [c] The original preparation of OsF_7 could not be reproduced,[3] but computations suggest its existence.[4] [d] Quantum-chemical calculations showed that the most likely species studied by experiment was $AuF_5 \cdot F_2$, and Au^{VII} remains inaccessible.[8,9]

For the 3d and 4d elements, oxidation state +VII is represented mainly by oxides or oxyfluorides of manganese and technetium, respectively (Table 1), and by the anions $[OsO_4]^-$ and $[RuO_4]^-$. Additionally, the trioxoorganorhenium complexes $RReO_3$ (for reviews, see refs 10 and 11) and a

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few Tc analogues[12] should be mentioned (Mn analogues have been addressed computationally[13]).

Given the well-known stability of ReF_7,[1] technetium heptafluoride, TcF_7, appears the most likely candidate for a heptafluoride of the lighter transition metals. The highest experimentally established technetium fluoride at the current time is TcF_6.[14] Here we address the possible existence of high-valent homoleptic technetium fluorides by state-of-the-art quantum chemical calculations. Energetics of relevant gas-phase elimination and homolytic bond-breaking reactions will be evaluated as well as activation barriers for key reactions.

2. Computational Methods

Structures were optimized using the density functional theory (DFT) level with the B3LYP[15−18] hybrid functional, using the Gaussian03[15] program. Transition-state optimizations were done using synchronous transit-guided quasi-newton methods[19,20] according to the QST2 and QST3 keywords implemented in Gaussian03. Optimizations were followed by single-point energy calculations at DFT (B3LYP) and high-level coupled-cluster (CCSD and CCSD(T)) levels (see below). A quasirelativistic energy-adjusted, small-core "Stuttgart-type" pseudopotential (effective-core potential, ECP) was used for technetium. The corresponding (8s7p6d)[6s5p3d] valence basis set was augmented by one f-type polarization function[21] (exponent α: 1.134). Energy-adjusted 8-valence-electron pseudopotentials and (6s6p3d1f)/[4s4p3d1f] valence basis sets were used for the noble-gas atoms Ng = Kr, Xe.[22]

Table 2. Optimized Structural Parameters (B3LYP) for Stationary Points on the TcF_7 Potential Energy Surface[a]

TcF_7 (C_1)		TcF_7 (C_{2v})		TcF_7 (C_{3v})	
$Tc-F_1$	181.2	$Tc-F_1$	186.8	$Tc-F_1$	185.1
$Tc-F_2$	181.1	$Tc-F_2$	184.6	$Tc-F_2$	183.7
$Tc-F_3$	186.0	$Tc-F_3$	184.6	$Tc-F_3$	185.0
$Tc-F_4$	186.2	$Tc-F_4$	183.8	$Tc-F_4$	185.1
$Tc-F_5$	186.2	$Tc-F_5$	183.8	$Tc-F_5$	183.7
$Tc-F_6$	186.1	F_1-Tc-F_2	142.6	F_1-Tc-F_2	152.5
$Tc-F_7$	186.0	F_1-Tc-F_4	77.8	F_1-Tc-F_4	131.6
F_1-Tc-F_2	177.8	F_2-Tc-F_3	74.8	F_2-Tc-F_3	75.9
F_3-Tc-F_4	72.3	F_2-Tc-F_4	76.9	F_2-Tc-F_4	78.5
F_4-Tc-F_5	72.3	F_4-Tc-F_5	93.7	F_4-Tc-F_5	78.5
F_5-Tc-F_6	72.4				
F_6-Tc-F_7	72.4				
F_7-Tc-F_3	72.4				
F_1-Tc-F_6	96.0				
F_2-Tc-F_6	85.3				

[a] Bond lengths in pm and angles in degrees. Cf. Figure 1.

Table 3. Computed Reaction Energies (in kJ mol^{-1})[a]

reaction	B3LYP[b]	CCSD(T)[c]
(a) $TcF_7 \rightarrow TcF_5 + F_2$	154.6 (127.6)	124.1
(b) $TcF_7 \rightarrow TcF_6 + F$	66.8 (47.9)	61.4
(c) $TcF_5 + KrF_2 \rightarrow TcF_7 + Kr$	−190.2	−185.1
(d) $TcF_5 + XeF_2 \rightarrow TcF_7 + Xe$	−57.4	−34.6
(e) $[TcF_6]^- + [KrF]^+ \rightarrow [TcF_6][KrF]$	−523.5	
(f) $[TcF_6]^- + [XeF]^+ \rightarrow [TcF_6][XeF]$	−459.9	
(g) $[TcF_6][KrF] \rightarrow TcF_7 + Kr$	−199.1	
(h) $[TcF_6][XeF] \rightarrow TcF_7 + Xe$	−95.2	
(i) $[TcF_6]^+ \rightarrow [TcF_4]^+ + F_2$	259.7	185.4
(j) $[TcF_6]^+ \rightarrow [TcF_5]^+ + F$	194.5	238.7
(k) $2[TcF_6]^+ \rightarrow 2[TcF_5]^+ + F_2$	233.8	218.0
(l) $KrF_2 \rightarrow Kr + F_2$[d]	−35.7	−60.9
(m) $F_2 \rightarrow 2F$[e]	155.3	152.7

[a] Reaction energies for singlet TcF_7, doublet TcF_6, triplet TcF_5, and singlet $[TcF_6]^+$. [b] Values in parentheses are counterpoise and zero-point vibration corrected values obtained with DZ+P basis on fluorine. [c] T_1-dignostics: TcF_7 (0.0289), TcF_6 (0.0294), $[TcF_6]^+$ (0.0315), TcF_5 (0.0263), $[TcF_5]^+$ (0.0299), $[TcF_4]^+$ (0.0292). [d] The experimental value is -60.2 ± 3.4 kJ mol^{-1}.[71] [e] The experimental value is $+154.56$ kJ mol^{-1}.[72]

In the optimizations, a fluorine DZ+P all-electron basis set by Dunning[23] was used. Stationary points on the potential energy surface were characterized by harmonic vibrational frequency analyses at this level using the isotopic mass of 98.9 u (providing also zero-point energy corrections to the thermochemistry). The subsequent single-point energy calculations had the fluorine basis replaced by a larger triple-ζ correlation consistent basis set (aug-cc-pVTZ).[24] The post-HF calculations were carried out with the MOLPRO 2002.6[25] program package. Basis-set superposition errors (BSSE) were estimated by the counterpoise (CP)[26,27] procedure. The importance of nondynamical correlation in coupled-cluster calculations was assessed by computing the T_1-diagnostic.[28,29] In all cases, the values obtained were sufficiently small to suggest essentially single-reference character of the wave functions (cf. footnote c in Table 3). Note that the methodology used here, in particular B3LYP optimizations followed by B3LYP or CCSD(T)

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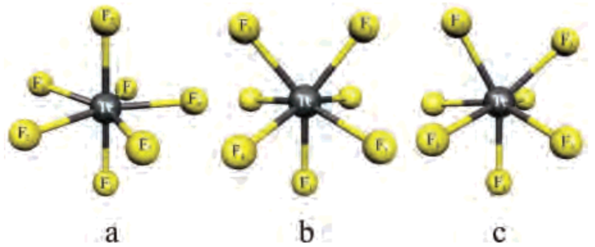

Figure 1. Stationary points on the TcF_7 potential energy surface (B3LYP results, singlet ground state). Bond lengths and angles are in Table 2. (a) Distorted pentagonal bipyramidal minimum with C_1 symmetry. (b) Monocapped trigonal prismatic minimum with C_{2v} symmetry. (c) Monocapped octahedral stationary point (degenerate imaginary frequency) with C_{3v} symmetry.

single-point energy calculations with larger ligand basis sets, are well established as a reliable tool for high-oxidation-state redox thermochemistry in the 5d transition-metal series, e.g., in previous studies on Hg, Au, Pt, Ir, and Os systems.[4,5,8,9,30] We do not consider spin−orbit corrections in this work. Our previous studies indicated spin−orbit effects to have only a minor influence on the relevant thermochemical data or activation barriers, even when open-shell 5d species were involved.[5]

3. Results

Structures. B3LYP-optimized structures of three stationary points on the TcF_7 potential energy surface (PES) are shown in Figure 1. Two minima were located. One is a distorted pentagonal bipyramidal structure without symmetry. The lack of symmetry is due to some puckering of the fluorine ligands in the basal plane. The regular pentagonal bipyramid (D_{5h}) is a transition state, less than 2 kJ mol^{-1} higher in energy. The other minimum is a monocapped trigonal prism with C_{2v} symmetry. The energies of the two minima differ only by around 1 kJ mol^{-1}. A singly capped distorted octahedron with C_{3v} symmetry (Figure 1) is an interconversion saddle point, which is also only 1.4 kJ mol^{-1} above the distorted pentagonal bipyramidal minimum (with a degenerate imaginary frequency at i35.0 cm^{-1}). TcF_7 is thus likely a fluctional molecule.

The next lower homoleptic fluoride TcF_6 is experimentally well-known.[14,31−35] B3LYP-optimizations provide a slightly compressed octahedron with C_s symmetry (Figure 2). Deviations from D_{4h} symmetry are mainly due to distortions of the equatorial bond angles. However, a regular octahedral transition state is only ca. 1 kJ mol^{-1} higher, indicating only a marginal static Jahn−Teller distortion of this doublet d^1 system. For more detailed discussion of transition-metal hexafluorides, see ref 14.

TcF_5 exhibits a (triplet) trigonal bipyramidal minimum with D_{3h} symmetry (Figure 2). A quadratic pyramidal structure (C_{4v} symmetry) was located to be a second triplet minimum, 38.5 kJ mol^{-1} above the D_{3h} minimum (the transition state for interconversion between the two minima appears surprisingly at rather high energies −208.6 kJ mol^{-1} above the D_{3h} minimum at the B3LYP level). The lowest singlet state exhibits C_{2v} symmetry and is 99.4 kJ mol^{-1} above the triplet ground state. Precise experimental structure determinations for TcF_5 are lacking at the current time,[36] and only a few rough indications are available.[33,37−39]

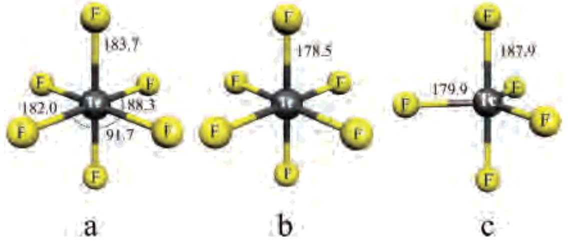

Figure 2. B3LYP-optimized minimum structures (bond lengths in pm and angles in deg). (a) Doublet TcF_6, distorted octahedral structure (C_s symmetry). (b) Singlet $[TcF_6]^+$ (O_h symmetry). (c) Triplet TcF_5, trigonal bipyramidal structure (D_{3h} symmetry).

Thermochemical Stability. Computed energies for the fluorine elimination reaction $TcF_7 \rightarrow TcF_5 + F_2$ and for homolytic bond breaking $TcF_7 \rightarrow TcF_6 + F$ are summarized in Table 3. As indicated in Computational Details, the chosen computational protocol (B3LYP and CCSD(T) single points at B3LYP optimized structures) has been established to provide rather accurate thermochemical data for this type of reactions, even though nondynamical correlation effects are non-negligible. The good performance of B3LYP in this area, which is notable in view of an apparently nonuniform quality of B3LYP in other areas of transition-metal thermochemistry,[40] is confirmed by the reasonable agreement with the CCSD(T) data (Table 3).

Unimolecular gas-phase elimination of F_2 from TcF_7 is predicted to be appreciably endothermic (by significantly more than 100 kJ mol^{-1}; Table 3). The second potential channel for gas-phase decomposition of TcF_7 involves the homolytic dissociation of a Tc−F bond to give TcF_6. This reaction is also calculated to be endothermic by about 60−70 kJ mol^{-1}. These results suggest appreciable stability of TcF_7 under typical gas-phase conditions.

Oxidation of TcF_5 by the endothermic fluorine compound KrF_2 is substantially exothermic (Table 3). This holds even more so when using one of the strongest presently known oxidative fluorinating agents, KrF^+.[41] Formation of the [KrF]-$[TcF_6]$ ion-pair complex from (gas-phase) $[KrF]^+$ and $[TcF_6]^-$ is highly exothermic and provides a local minimum on the potential energy surface. However, the complex is calculated to decompose also rather exothermically into TcF_7 and Kr (note that these energies will be generally somewhat more positive in the condensed phase due to electrostatic stabilization of the ion-pair complexes). This holds even so for the corresponding xenon ion-pair complex $[XeF][TcF_6]$, which

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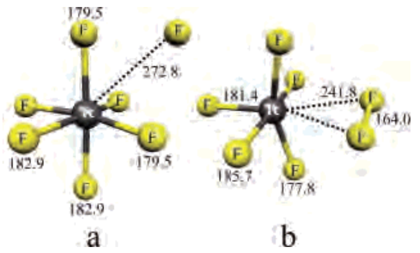

Figure 3. B3LYP-optimized transition states (distances in pm). (a) TS for homolytic bond breaking (C_{3v} symmetry) in TcF_7. (b) TS for concerted F_2 elimination from TcF_7 (C_{2v} symmetry).

Figure 4. B3LYP-optimized transition state for the bimolecular reaction $2TcF_7 \rightarrow 2TcF_6 + F_2$ (distances in pm).

still decomposes with appreciable exothermicity. Experimental attempts to prepare the precursor $[TcF_6]^+$ from TcF_6 and KrF^+ have been unsuccessful,[42] indicating the practical experimental difficulties in this area (see below).

Bimolecular elimination of F_2, $2TcF_7 \rightarrow 2TcF_6 + F_2$, is calculated to be slightly exothermic (by -15.2 kJ mol^{-1} at the B3LYP level) but has a substantial barrier (see below).

Transition States and Activation Barriers for Decomposition of TcF_7. Figure 3 shows the transition states for both homolytic bond breaking and for concerted elimination of F_2. Homolytic bond breaking goes via a singly capped octahedral transition state (C_{3v} symmetry), where the cap represents the Tc−F bond to be broken. The imaginary frequency is computed to be i316 cm^{-1} at the B3LYP level. The barrier amounts to appreciable 198.3 kJ mol^{-1}. The large barrier arises from substantial nuclear reorganization, as we have discussed previously for closely related cases.[4,5] The transition state for concerted F_2 elimination exhibits C_{2v} symmetry and has its imaginary frequency at i249 cm^{-1}. The formation of an F_2 molecule and of D_{3h} TcF_5 is already visibly on its way (Figure 3). The barrier is computed to be even larger than for homolytic bond breaking, 296.9 kJ mol^{-1} at the B3LYP level. These results suggest thus not only thermochemical stability for all important unimolecular decomposition pathways but also large kinetic stability.

We have been able to locate also the transition state for the bimolecular reaction $2TcF_7 \rightarrow 2TcF_6 + F_2$. It has C_{2v} symmetry (Figure 4), and the imaginary frequency is computed to be i395.9 cm^{-1}. Figure 4 shows clearly the breaking of two Tc−F bonds with simultaneous formation of F_2. The computed activation barrier is again appreciable, 254.6 kJ mol^{-1} at the B3LYP level.

The Cation $[TcF_6]^+$. The cation $[TcF_6]^+$ might accept a fluoride anion and thus be a precursor on the way to TcF_7. The current lack of success in preparing this cation appears closely related to the absence of TcF_7. It appears thus important to evaluate also the thermochemistry of the $[TcF_6]^+$ cation, apart from it being an interesting target in its own right. Its 5d homologue $[ReF_6]^+$ has been synthesized in the reverse way, by reacting ReF_7 with strong fluoride ion acceptors.[43] Other successful routes via oxidation of ReF_6 are known.[44] On the other hand, fluorination of Tc^{VII} oxyfluorides with KrF_2 ends at $TcOF_5$, and neither TcF_7 nor $[TcF_6]^+$ have been obtained in this way.[42] Even fluorinating oxidation of TcF_6 by $[KrF]^+[AsF_6]^-$ did not give $[TcF_6]^+[AsF_6]^-$.[42]

As expected, B3LYP optimization provides a regular octahedral singlet ground state for $[TcF_6]^+$ (with a Tc−F bond length of 178.5 pm; cf. Figure 2). The regular trigonal prismatic transition state (D_{3h}) for Baylar twist lies at 45.9 kJ mol^{-1}, with an imaginary frequency at i86 cm^{-1}. This is in the range of other d^0 hexafluorides.[45,46] Both relevant unimolecular decomposition channels of (gas-phase) $[TcF_6]^+$, concerted F_2 elimination and homolytic Tc−F bond breaking, are computed to be strongly endothermic (cf. Table 3). This suggests stability as isolated gas-phase entity. Even the bimolecular F_2 elimination is very endothermic (Table 3). The adiabatic ionization potential $TcF_6 \rightarrow [TcF_6]^+$ is calculated to be appreciable 11.8 eV at the CCSD(T) level. In the condensed phase, the $[KrF][TcF_6]$ ion-pair complex is expected to decompose exothermically into TcF_7 and Kr (see above and Table 3).

4. Conclusions

This quantum chemical study indicates strongly that TcF_7 is a viable target for preparation and would provide the first heptafluoride of a 4d element. All unimolecular decomposition pathways are appreciably endothermic and moreover exhibit large activation barriers. While the bimolecular F_2 elimination is slightly exothermic, it has also been computed to exhibit a high activation barrier.

Why then has TcF_7 not yet been observed experimentally? We think that this is largely related to practical difficulties of the usual synthetic approaches. Oxidative fluorination of oxo complexes is rendered very difficult by the rather pronounced oxophilicity of Tc^{VII}.[42] While this does not entirely rule out a traditional chemical synthesis at elevated temperatures and pressures like it is possible for ReF_7,[47-72]

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an approach via gas-phase-like conditions appears the safer way toward this interesting heptafluoride. This may be done, for example, by matrix-isolation spectroscopy. Notably, TcF_7 is predicted to be a fluxional molecule, as indicated by two low-lying minima of distorted pentagonal bipyramidal and capped trigonal prismatic structures, linked by low-lying transition states for pseudorotation.

Note added in proof: TcO_3F has now been characterized in the solid state (Supeł, J.; Abram, U.; Hagenbach, A.; Seppelt, K. *Inorg. Chem.*, Web Release Date: June, 5, 2007).

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