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Applications of noble-gas chemistry to the synthesis of high-valent metal oxofluoride species

W.J. Casteel, Jr., N. LeBlond, P.E. Lock, H.P.A. Mercier, D.M. MacLeod, G.J. Schrobilgen *

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

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New high-valent metal oxofluoride species are described which rely exclusively, or in part, upon noble-gas fluorides for their geneses. Clean routes to the preparation of a number of high-valent metal oxofluoro

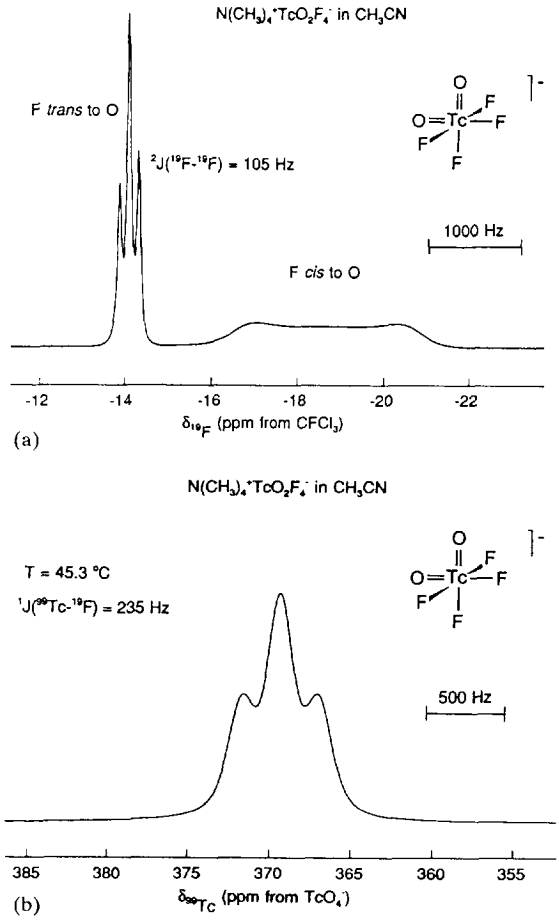

Fig. 1. ^{19}F NMR spectrum (a) and ^{99}Tc NMR spectrum (b) of $[N(CH_3)_4]^+[TcO_2F_4]^-$ in CH_3CN solvent.

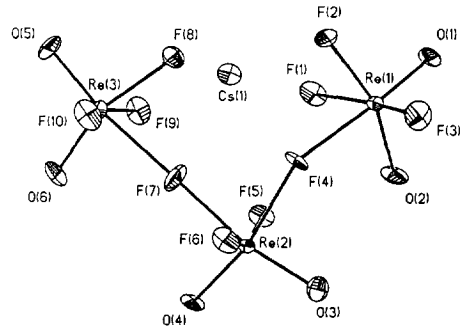

Fig. 2. ORTEP diagram of $Cs^+[Re_3O_6F_{10}]^-$.

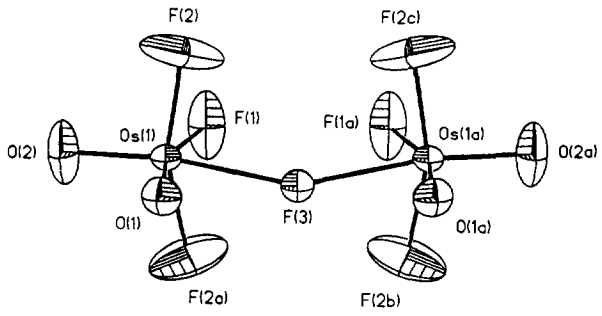

Fig. 3. ORTEP diagram of $[Os_2O_4F_7]^+[Sb_2F_{11}]^-$.

species are afforded by the strong oxidant fluorinators XeF_6 and KrF_2. Reaction in anhydrous HF with a metal oxide or oxofluoride in which the metal is already in its highest oxidation state in anhydrous HF leads to fluorination by means of oxide/fluoride metatheses in the case of XeF_6 or by oxidative elimination of O_2 in the case of KrF_2. Fluoride/oxide metathesis reactions between M_2O_7 (M = Tc or Re) and XeF_6 afford high-yield and high-purity syntheses of TcO_2F_3 (the second

* Corresponding author.

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example of a Tc^{VII} oxofluoride) and ReO_2F_3 as an improved synthesis. The crystal structure of TcO_2F_3 has been described recently and consists of an open-chain, fluorine-bridged structure in which the fluorine bridges are *trans* to the oxygens and the oxygens are *cis* to one another [1]. Fluorination of TcO_2F_3 with KrF_2 has provided preliminary evidence for $TcOF_5$.

The fluoride ion donor/acceptor properties of TcO_2F_3 and ReO_2F_3 have been explored leading to the syntheses of the novel anions *cis*-$[TcO_2F_4]^-$ ($[XeF_5]^+$, Li^+, Cs^+ and $[N(CH_3)_4]^+$ salts; see NMR spectra, Fig. 1), $[Re_3O_6F_{10}]^-$ (Cs^+ salt; Fig. 2) and a fuller characterization of the previously known [2] *cis*-$[ReO_2F_4]^-$ anion (Li^+, Na^+, $[N(CH_3)_4]^+$ salts). The $[TcO_2F_2]^+$ and $[ReO_2F_2]^+$ cations have been stabilized as their $[AsF_6]^-$ and $[SbF_6]^-$ salts, and characterized in solution by ^{19}F and ^{99}Tc NMR spectroscopy and in the solid state by vibrational spectroscopy.

The synthesis from pure ReO_2F_3 by reaction with a stoichiometric amount of $B(OTeF_5)_3$ has afforded $ReO_2(OTeF_5)_3$ and its full characterization by low temperature ^{19}F and ^{125}Te NMR spectroscopy. The structure is consistent with a trigonal bipyramidal arrangement of ligand atoms in which the oxygen atoms occupy the equatorial plane. At higher temperatures, the $OTeF_5$ groups undergo intramolecular exchange by means of a pseudo-rotation mechanism. The interaction of $ReO_2(OTeF_5)_3$ with a stoichiometric amount of $[N(CH_3)_4]^+[OTeF_5]^-$ yields the *cis*-$[ReO_2(OTeF_5)_4]^-$ anion which has been characterized by ^{19}F and ^{125}Te NMR spectroscopy and Raman spectroscopy.

Recently, *cis*-OsO_2F_4 has been synthesized in HF solvent by the reaction of KrF_2 with OsO_4 [3] and fully characterized [4]. In the present work, *cis*-OsO_2F_4 has been shown to behave as a fluoride-ion donor towards AsF_5 and SbF_5 in HF solvent, leading to the isolation and characterization of $[Os_2O_4F_7]^+[Sb_2F_{11}]^-$ by X-ray crystallography (Fig. 3). The $[Os_2O_4F_7]^+$ cation is a *cis*-dioxo structure in which the bridging fluorine is *trans* to the oxygen atoms.

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