Review of technetium chemistry research conducted at the University of Nevada Las Vegas

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Abstract The chemistry of technetium is being explored at the University of Nevada Las Vegas. Our goal is to investigate both the applied and fundamental aspects of technetium chemistry, with a special emphasis on synthesis, separations, and materials science. The synthetic chemistry focuses on metal–metal multiple bonding, oxides and halides. Synthesis and characterizations of $(n\text{-}Bu_4N)_2Tc_2X_8$, $Tc_2(O_2CCH3)_4X_2$ ($X = Cl$, Br), TcO_2, $Bi_2Tc_2O_7$, Bi_3TcO_8, $TcBr_3$ and $TcBr_4$ have been performed. The applied chemistry is related to the behavior of Tc in the UREX process. Separation of U/Tc has been conducted using anion exchange resin and metallic Tc waste form synthesized and characterized.

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Introduction

Technetium, element 43, occupies a central position in the Periodic Table. It is the lowest atomic number radioelement and thirty four unstable isotopes of the element are known with mass numbers ranging from 85 to 118. The most readily available isotope is ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ y, $\beta_{max} = 292$ keV) which is present in large quantities from spent nuclear fuel ($\sim 6\%$ of the fission yield). The coordination chemistry of technetium, spanning oxidation states from $+7$ to -1, is similar to but not nearly as extensive as that of its heavier congener rhenium. The chemistry of technetium is being explored at the Harry Reid Center for Environmental Studies, UNLV. The facilities at the Harry Reid Center include modern radiochemistry laboratories where investigators can work with multi-milligram quantities of ^{99}Tc, and analytical instrumentation dedicated for radioelement characterization and analysis. Our goal is to investigate both the applied and fundamental aspects of technetium chemistry, with a special emphasis on synthesis, separations, and materials science. The fundamental chemistry focuses on metal–metal multiple bonding, oxides and halides. The applied chemistry is related to the UREX process, especially the separation of uranium/technetium and synthesis of Tc containing waste forms. In this article, we summarize the work performed at UNLV on Tc chemistry over the past 4 years; we also present new experimental and theoretical results on technetium trioxide, heterobimetallic complexes and Tc–Zr alloys.

Experimental

Chemical

The starting material NH_4TcO_4 was obtained from the Oak Ridge Isotope Office. Tc metal was prepared by thermal decomposition of NH_4TcO_4 at 700 °C under and H_2/Ar atmosphere. Technetium heptoxide was obtained after oxidation of TcO_2 in an oxygen atmosphere at 450 °C.

Diffraction

The XRD patterns were obtained using a Philips PANalytical X'Pert Pro instrument with a Cu-Kα target and a Ni filter.

Microscopy

SEM imaging was performed on a JEOL scanning electron microscope model JSM-5610 equipped with secondary electron and backscattered electron detectors.

Calculations

First-principles all-electron calculations of the total energies and optimized geometries were performed using the spin-polarized density functional theory as implemented in the DMol3 software [1]. The exchange correlation energy was calculated using the generalized gradient approximation (GGA) and local density approximation (LDA). 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 a p-type polarization function added to hydrogen and d-type polarization functions added to heavier atoms. 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) without symmetry constraints with an energy convergence tolerance of 10^{-5} Hartree and a gradient convergence of 2×10^{-3} Hartree/Bohr.

Results and discussion

Multiply metal–metal bonded

Technetium dimers containing a quadruple metal–metal bond are a relatively new addition to the family of Tc compounds and are interesting from the point of view of structure and bonding. As reported in a recent monograph

[2], only five technetium quadruply bonded dimers have been characterized structurally. Recently, reliable syntheses of (n-Bu$_4$N)$_2$Tc$_2$X$_8$ and Tc$_2$(O$_2$CCH$_3$)$_4$X$_2$ (X = Cl, Br) were developed in our laboratory which led to X-ray Absorption Fine Structure Spectroscopy (XAFS), UV–Vis and X-ray Diffraction (XRD) studies aimed at elucidating the structures and spectroscopic properties of these compounds [3, 4]. The tetracarboxylate complexes were analyzed by XAFS spectroscopy while the structure of (n-Bu$_4$N)$_2$Tc$_2$Br$_8$ was solved by single crystal XRD [5]. The new structural parameters permitted to study the influence and position of the ligand on the Tc–Tc separation. The Tc–Tc separation in Tc$_2$(O$_2$CCH$_3$)$_4$X$_2$ (X = Cl, Br) is the largest noted among all the quadruply bonded Tc dimers whose structures have been determined. This phenomenon is due to the presence of strong axial ligands which weaken the Tc–Tc σ-bond and increase the Tc–Tc separation. The nature of the axial ligand also has an influence on the Tc–Tc separation. A longer Tc–Tc separation in Tc$_2$(O$_2$CCH$_3$)$_4$X$_2$ (X = Cl, Br) than in Tc$_2$(O$_2$CCH$_3$)$_4$(TcO$_4$)$_2$ indicates that axial chloride and bromide ligands are better σ-donors and exert a greater influence on the Tc–Tc quadruple bond than the axial pertechnetate ligand. We further investigated the electronic spectra of the $M_2Cl_8^{2-}$ and $M_2Br_8^{2-}$ (M = Tc, Re). The similarity of the optical spectra and electronic structures in those compounds permitted the assignment of several previously unassigned transitions in the Tc$_2$X$_8^{2-}$ spectra [3].

The coordination chemistry of heterobimetallic technetium complexes is poorly developed: currently only two compounds have been synthesized (i.e., TcMn(CO)$_{10}$ and TcRe(CO)$_{10}$) [6]. To further investigate metal–metal bonding chemistry of technetium, theoretical calculations on technetium-bearing heterometallic molecules have been carried out. Several compounds were investigated and CrTcCl$_9^{3-}$, ReTcCl$_8^{2-}$, MoTcCl$_4$(PMe$_2$Ph)$_4$ (Fig. 1) are among the new heterometallic systems predicted to be stable from first-principles calculations. These compounds can be synthesized using similar procedures reported for their homologues [7, 8].

Technetium oxides

The oxide chemistry of technetium is poorly studied. Only two binary oxides are known: TcO_2 and Tc_2O_7 whose structure and properties are still not well understood. Our recent studies have permitted a better understanding of the structure of binary and ternary Tc oxides: the crystalline structure of TcO_2 was determined by neutron powder diffraction and density functional theory (DFT) calculations were performed in order to elucidate the bonding mechanism in TcO_2 [9]. Concerning Tc_2O_7, a convenient preparation route has been developed.

Fig. 1 Optimized geometries of (**a**) $CrTcCl_9^{3-}$, (**b**) $ReTcCl_8^{2-}$, and (**c**) $MoTcCl_4(PMe_2Ph)_4$. $TcCrCl_9^{3-}$: Tc–Cl: 2.384 Å; Tc–Cl(bridge): 2.420 Å; Cr–Cl: 2.310 Å; Cr–Cl(bridge): 2.397 Å. $TcReCl_8^{2-}$: Tc–Re: 2.200 Å; Tc–Cl: 2.330 Å; Re–Cl: 2.307 Å. $MoTcCl_4(PMe_2Ph)_4$: Tc–Mo: 2.184 Å; Tc–Cl: 2.378 Å; Tc–P: 2.464 Å, 2.479 Å; Mo–Cl: 2.381 Å; Mo–P: 2.381 Å, 2.390 Å

(a) $CrTcCl_9^{3-}$

(b) $ReTcCl_8^{2-}$

(c) $MoTcCl_4(PMe_2Ph)_4$
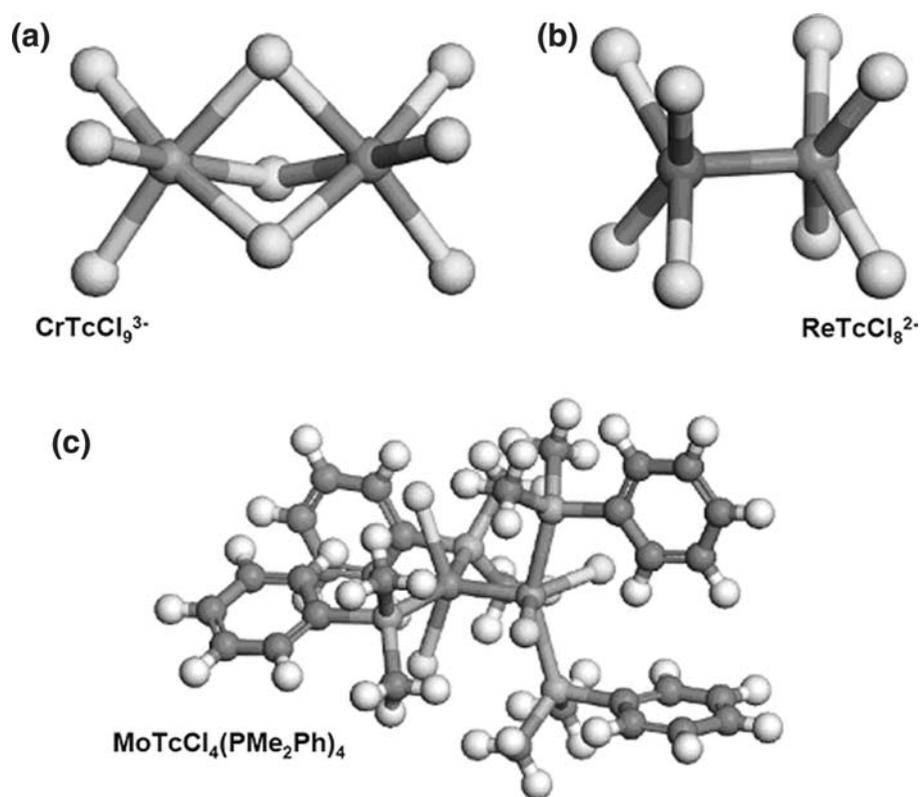
Ternary oxides of technetium with a post-transition element were never pursued with the exception of the compound $PbTcO_3$. Our first study of Tc ternary system focused on bismuth containing oxides and two new phases were synthesized and characterized: $Bi_2Tc_2O_7$ (cubic pyrochlore-type structure) and Bi_3TcO_8 (cubic fluorite-type structure) [10]. In $Bi_2Tc_2O_7$, the Tc(IV) cations are octahedrally coordinated, whereas in Bi_3TcO_8 the Tc(VII) cations are tetrahedrally coordinated. On the basis of structural similarities between $Bi_2Tc_2O_7$ and closely related oxides, $Bi_2Tc_2O_7$ is expected to be a metallic oxide with Pauli paramagnetism. Electronic structure calculations support metallic conductivity for $Bi_2Tc_2O_7$ and insulating behavior for Bi_3TcO_8.

An important work was the elucidation of TcO_3. Technetium trioxide has been identified in the vapor phase but has not been positively identified as a crystalline solid [11]. Theoretical calculations suggest that the solid should be stable below 500 K, after which it disproportionates to TcO_2 and Tc_2O_7 [12]. To further investigate stability and formation of TcO_3, DFT calculations were performed. All-electron scalar relativistic calculations based on DFT indicate that, isostructural with ReO_3, TcO_3 crystallizes at 0 K in the space group P*m*-3*m*, with a lattice constant of 3.88 Å (Fig. 2). Ab initio molecular dynamics simulations performed in a unit cell using the DMol3 code further suggest that TcO_3 rapidly becomes unstable at temperatures as low

as 200 K, with a structural transition from the P*m*-3*m* to the R3 space group.

Attempts to make TcO_3 via different method were tested. Technetium heptoxide was used as a precursor and two reactions were tested: (i) thermal decomposition of Tc_2O_7 dioxane adduct at 130 °C under Ar atmosphere and (ii) reaction between Tc_2O_7 and SO_2 gas at 125 °C. The first method was successfully tested with rhenium, and thermal decomposition of Re_2O_7–dioxane adduct lead to ReO_3 [13]. For technetium, XRD analysis of the product obtained by the thermal reaction of Tc_2O_7–dioxane adducts shows the presence of TcO_2 as the major phase. The second method has been reported, and reaction between Tc_2O_7 and SO_2 was expected to produce a purple metallic compound: TcO_3 [14]. We examined this method; the reaction product was a black amorphous compound, analyses by cerium titration indicate an average oxidation degree of 5.1. This result was inconclusive as the compound can be a mixture of Tc oxidation states between IV and VII and no purple metallic compounds were observed.

Binary halides

Because technetium and rhenium are members of the same group in the periodic table, the occurrence of analogous halides is expected. Thirteen binary phases have been reported for rhenium, but only three are known and well-
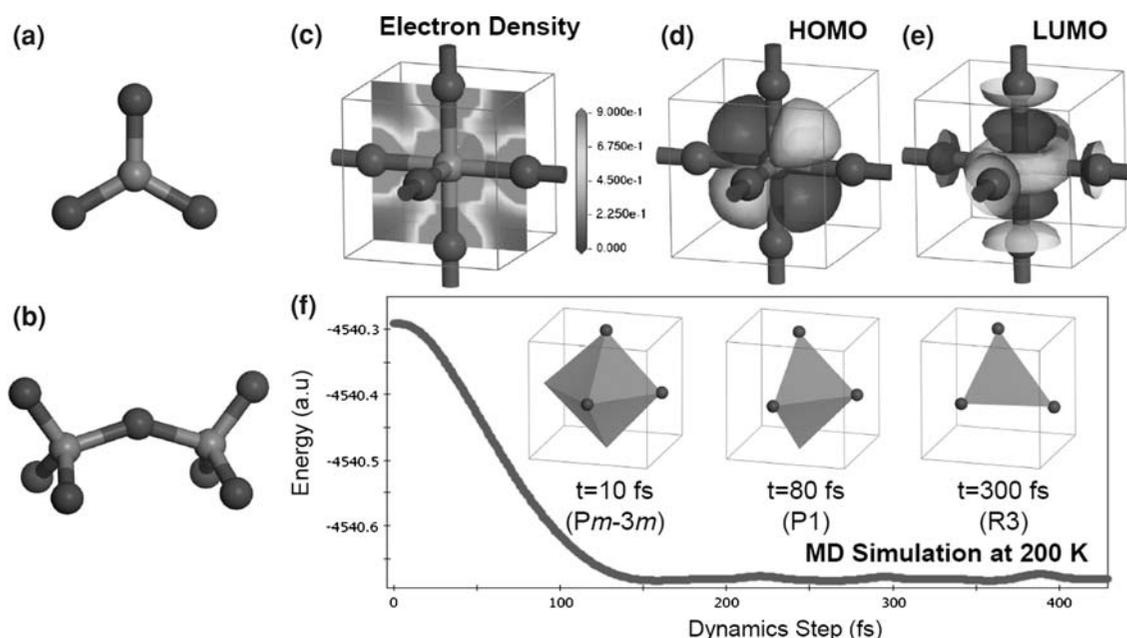
Fig. 2 Structures of (**a**) Tc_2O_7 and (**b**) TcO_2. Structure of TcO_3 calculated using all-electron scalar relativistic density functional theory: (**c**) Projected electronic charge density (in $e/\mathring{A}^3$); (**d**) Highest occupied molecular orbital. (**e**) Lowest unoccupied molecular orbital. (**f**) Molecular dynamics simulation of the structural evolution of TcO_3 at 200 K

characterized for technetium (TcF_6, TcF_5, and $TcCl_4$) [15]. Recently, we have synthesized $TcBr_3$ and $TcBr_4$ by reaction between Tc metal and elemental bromine [16]. Single crystal XRD measurements indicate that the structure of $TcBr_3$ consists of infinite chains of face-sharing $TcBr_6$ octahedra with a regular alternation of short and long Tc–Tc distances (2.8283(4) Å, 3.1434(4) Å). $TcBr_4$ contains infinite chains of edge-sharing $TcBr_6$ octahedra with no apparent metal–metal bond (Tc–Tc = 3.7914(4) Å). $TcBr_3$ is the first example of the TiI_3 structure prepared with a d^4 metal, and contributes towards understanding metal–metal bonding interactions for this structure type. The synthesis of technetium binary iodides was also investigated, Tc metal and elemental iodine were reacted at 400 °C in a sealed glass tube but no reaction occurred.

Technetium in the fuel cycle

In the U.S. advanced fuel cycle program, the UREX + 1 process is proposed to separate transuranic elements from spent nuclear fuel. The fission product ^{99}Tc will be extracted into an organic phase containing tributylphosphate together with uranium within the first process steps. Treatment of this stream requires the separation of U from Tc and the placement of the Tc into a suitable waste storage form. Past work on disposal forms for wastes from electrochemical processing of spent fuel from the decommissioned EBR-II reactor examined alloys of Tc with stainless steel and zirconium as potential disposal forms for Tc [17].

In the context of the demonstration of the UREX process, we performed separation of uranium and technetium using an anion exchange resin on a simulant solution containing 99 g/L of U and 130 mg/L of Tc [18]. After sorption on the resin, TcO_4^- was eluted with NH_4OH, the eluting stream was treated, and the technetium converted to Tc metal. The synthesis of Tc metal from the eluting solution was performed in three steps, evaporation of the solution to dryness, dissolution of the powder in water followed by the precipitation of TcO_4^- as $(n-Bu_4N)TcO_4$ and conversion of $(n-Bu_4N)TcO_4$ to Tc metal by steam reforming under argon according to published procedure [19]. The metal produced by this method was characterized by XRD, XAFS and transmission electron microscopy [20].

In order to investigate the development of metallic waste form, Tc metal was alloyed with Zr ($\sim$ 1:1) and characterized by SEM and XRD. The sample contains two phases: TcZr and Tc_2Zr as minor phase. The TcZr phase was identified as a beta-Zr-type solid-solution phase where $\sim$ 50% of the structure sites are occupied by Tc. Tc_2Zr crystallizes in the hexagonal space group $P6_3/mmc$. Rietveld analysis could confirm the $MgZn_2$ type structure previously reported [21]. To investigate the stability of this alloy, the sample was sintered at 1,500 °C for 60 h under Ar atmosphere with low presence of oxygen. XRD analysis after sintering indicates that Zr metal has oxidized to ZrO_2 while Tc remains under metallic form. Invariance of the unit cell volume of Tc metal and ZrO_2 indicate the absence of ZrO_2/TcO_2 or Zr–Tc solid solution. During this

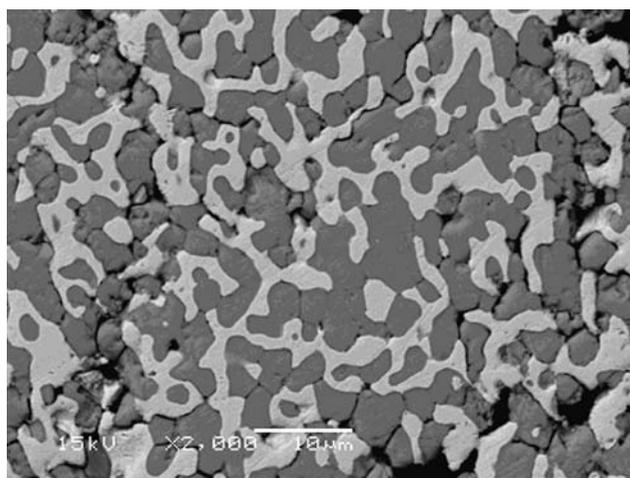**Fig. 3** SEM image (2,000×) of the TcZr alloy after oxidation at 1,500 °C. The dark phase was identified by EDAX as ZrO_2 and the white phase as Tc metal

oxidation, a phase separation between Tc and ZrO_2 has occurred (Fig. 3). From the results obtained, it appears that the stability of Tc–Zr alloys will be function of the stability of the Zr metal.

Conclusion

The technetium chemistry at the University of Nevada Las Vegas focuses on both fundamental and applied chemistry. During the past years, we developed convenient synthesis of $(n\text{-}Bu_4N)_2Tc_2X_8$, $Tc_2(O_2CCH3)_4X_2$ ($X = $ Cl, Br), TcO_2, Tc_2O_7, $TcBr_3$ and $TcBr_4$, and characterized their crystallographic and electronic structures. Those compounds, used as precursors, will allow the synthesis of new compounds (binary halides, oxide, quadruply bonded technetium(III) dimers) and advance understanding of the fundamental chemistry of technetium. Concerning the applied chemistry, we focused on the separation of uranium and technetium for the UREX process and synthesis and characterization of metallic waste forms. Laboratory scale demonstration of U/Tc separation using anionic exchange was successfully performed and Tc–Zr alloys synthesized. Future works on Tc chemistry include development and

characterization of Tc radiopharmaceutical complexes. Works along this line are in progress.

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