Synthesis and Characterization of Technetium Binary Chlorides: $TcCl_2$ and $TcCl_4$

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Outline

I. Introduction

II. Current Work

- $TcCl_2$ – Novel binary technetium halide
- $TcCl_4$
- Reduction of $TcCl_4$ to $TcCl_2$

III. Conclusions

Fundamental Chemistry of Technetium

Group VII Binary Halides

Rhenium

→12 known and well-characterized: ReX_3 (X = Cl, Br, I), ReX_4 (X = Cl, Br, I), ReX_5 (X = F, Cl, Br), ReX_6 (X = F, Cl), ReF_7

Technetium

→ Seven compounds known : TcF_6, TcF_5 , $TcCl_4$, $TcBr_4$, and $TcBr_3$, $TcCl_3$, and $TcCl_2$

→ Necessity for a better understanding of the fundamental chemistry of technetium (i.e. coordination chemistry, radiopharmaceuticals, waste forms, etc.)

Low-Valent Technetium Binary Halides

$TcCl_3$:

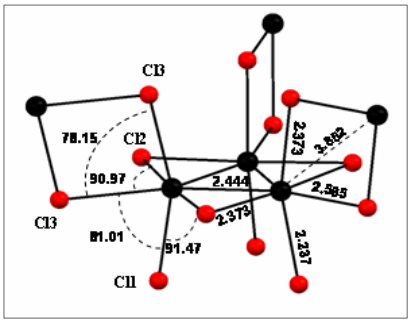
$Tc_2(O_2CCH_3)_4Cl_2$

T = 150 °C → HCl (g)

$Tc_2(O_2CCH_3)_2Cl_4$

T = 300 °C → HCl (g)

$TcCl_3$



Motivation: Re_3X_9 (X = Cl, Br, I)

Triangular Tc_3Cl_9 units with C_{3v} symmetry

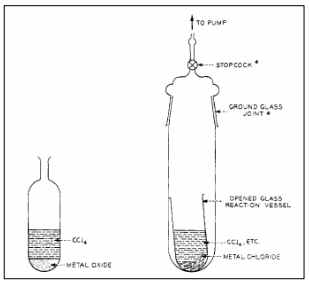
Isostructural to $ReCl_3$ (R-3m)

Tc-Tc separation (2.444 Å) indicates a Tc=Tc double bond

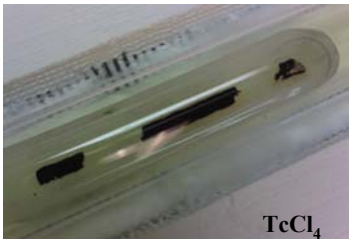
Technetium Tetrachloride

- **Synthesized from the reaction of technetium metal and flowing chlorine gas from 300-500 °C**
  - **Highest oxidation binary Tc chloride vs. $MoCl_5$ and $ReCl_6$**

R. Colton. *Nature*, 193, 872 (1962)



K. Knox and C. E. Coffey, *J . Amer. Chem. Sac., 1959, 81, 7.*



Low-Valent Technetium Binary Halides

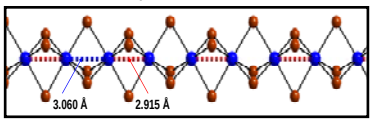
$TcBr_4$ and $TcBr_3$:

$M + (3/2)\ Br_2 \rightarrow MBr_3$ (M = Ru, Re, Mo)

→Synthesized via stoichiometric reaction of Tc metal with Br_2 (~ 1:3 and 1:4) in sealed Pyrex tube at elevated temperatures

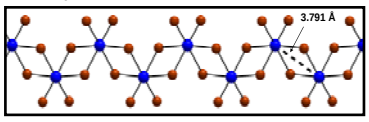
Tc Metal

→$TcBr_3$ - Infinite chains of face-sharing $TcBr_6$ distorted octahedra



*Poineau, F et al. *JACS*, 2009

→$TcBr_4$ - Infinite chains of edge-sharing $TcBr_6$ octahedra



*Poineau, F et al. *JACS*, 2009

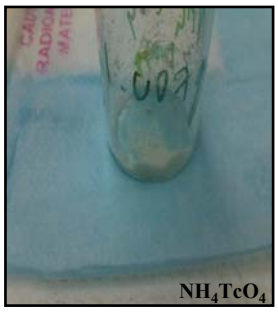
Purification of NH_4TcO_4

ORNL starting material impure (mix TcO_2/NH_4TcO_4)

1. **Dissolve in H_20 and NH_4OH/H_20_2**
2. **Evaporate to dryness using rotovap**

T = 80° C, H_20

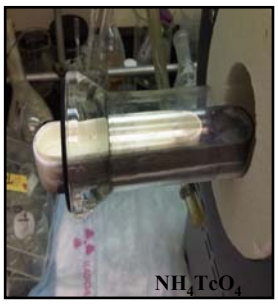
NH_4OH / H_2O_2



Synthesis of TcO_2

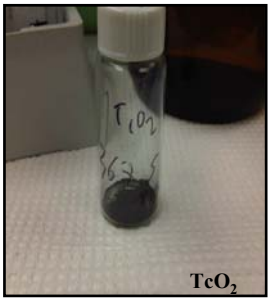
Reduction of Tc(VII) to Tc(IV)

$$NH_4TcO_4 \rightarrow TcO_2 + (1/2)\ N_2 + 2\ H_2O$$



T = 700° C, Ar (g)

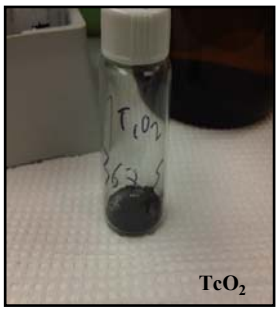
t = 2 hr



Synthesis of Technetium Metal

Hydrogen reduction of Tc(IV) to the metal

$$TcO_2 + 2\ H_2 \rightarrow Tc + 2\ H_2O$$



T= 700° C, H_2 (g)

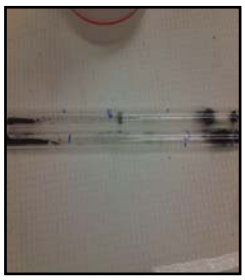
t = 2 hr

Synthesis of $TcCl_2$

Stoichiometric reaction of 1:2.5 mol Tc metal with chlorine gas produced black crystals of $TcCl_2$

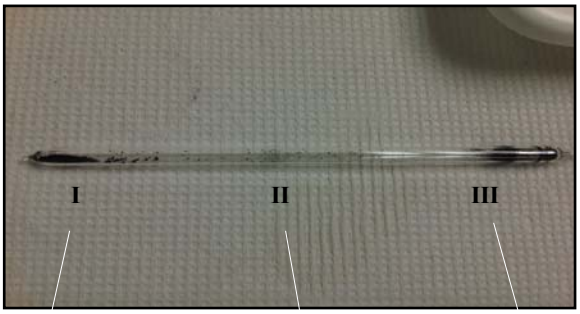
T= 450° C, Cl_2(g)

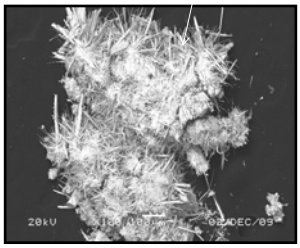
24 hr

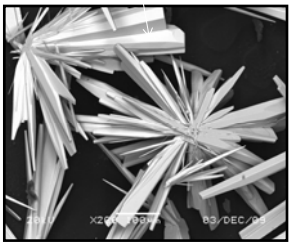


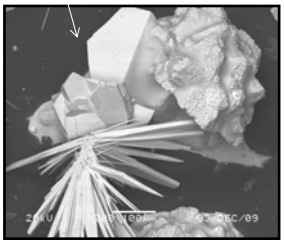
Compound insoluble in concentrated HCl and common organic solvents

SEM of $TcCl_2$

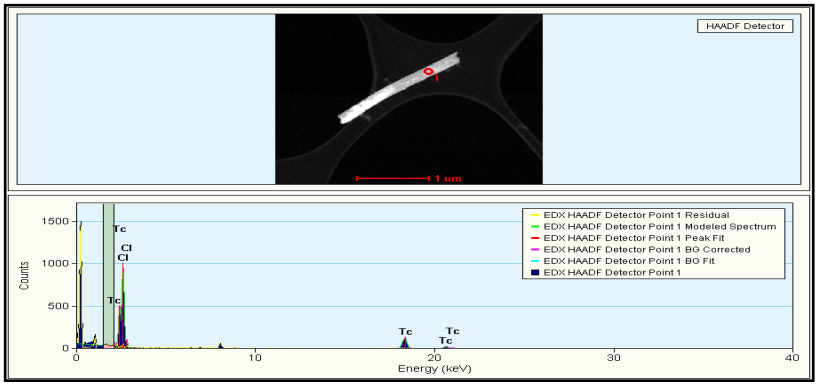








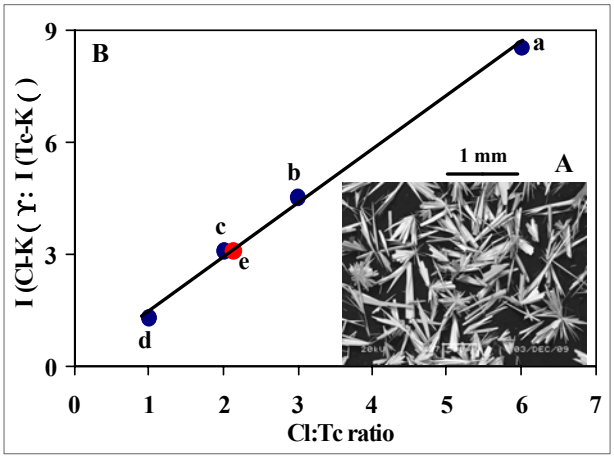
Energy Dispersive X-ray Spectroscopy (EDX)



Element	Weight %	Atomic %
Cl	43.177	67.746
Tc	56.822	32.253

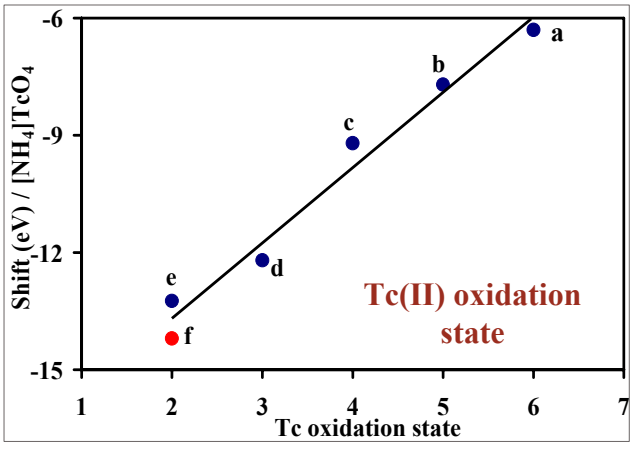
→ ~ 2 Cl: 1 Tc atom

EDX



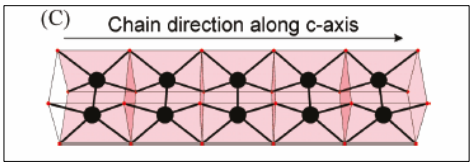
Plot of Intensity [Cl-K_a]/Intensity [Tc-K_a] vs. the [Cl:Tc] ratio for a) K_2TcCl_6, b) $TcCl_3(PPh_3)_2$·(MeCN), c) $Tc_2Cl_4(O_2CCH_3)_2$, d) $Tc_2Cl_2(O_2CCH_3)_4$, and e) $TcCl_2$ (red dot).

XANES as a Function of Oxidation State

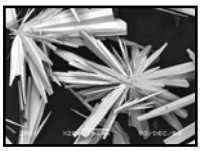


Chemical shift ΔE (eV) of Tc-K edge relative to NH_4TcO_4 versus formal oxidation state for a) (*n*-Bu_4N)$TcNCl_4$, b) (*n*-Bu_4N)$TcOCl_4$, c) $(Me_4N)_2TcCl_6$, d) (*n*-$Bu_4N)_2[Tc_2Cl_8]$, e) $Tc_2Cl_4(PMe_2Ph)_4$, and f) $TcCl_2$ (red dot).

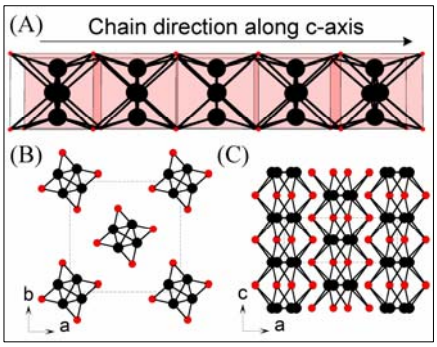
Single Crystal X-Ray Diffraction (SCXRD)



$TcCl_2$ Chain



$TcCl_2$ single-crystals with "sea urchin" motif grown by vapor phase transport with $AlCl_3$



Disordered model of $TcCl_2$

- Novel structure - Infinite chains of eclipsed $[Tc_2Cl_8]$ units running along *c* axis
- Eight Cl atoms (Tc-Cl = 2.372Å) form rectangular prism
- Tc-Tc triple bond (2.127 Å)
- Inter-chain disorder present

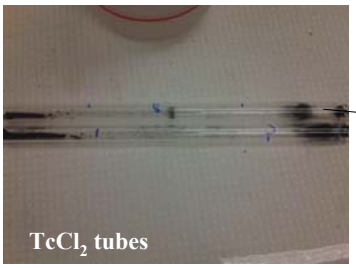
Summary of $TcCl_2$

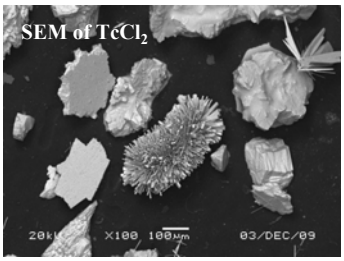
- Stoichiometric reaction of chlorine gas and technetium metal formed technetium dichloride with a new structure type
  - Reaction yields $TcCl_2$ and unreacted Tc metal
- Is there another method for synthesizing pure $TcCl_2$?

Formation $TcCl_2$ from $TcCl_4$

Thermal reduction of higher oxidation chlorides to low oxidation states, i.e. $Pt^{IV}Cl_4 \longrightarrow Pt^{II}_6Cl_{12}$ at 300 °C

M. Degner , et. al.., *Transition metal Chem..*, 1, 41 (1975).



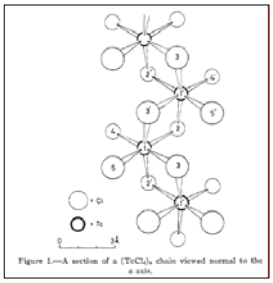


Does $TcCl_4$ decompose to $TcCl_2$?

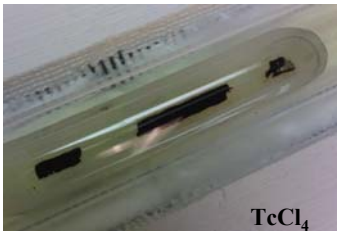
Technetium Tetrachloride

- **Synthesized from the reaction of technetium metal and flowing chlorine gas**
  - **Generation of technetium oxyhalides ($TcOCl_4$ and TcO_3Cl)**
  - **Presence of unreacted Tc metal**
  - **No optimized synthesis**
  - **Two different structural parameters**

→New synthetic method using sealed Pyrex tube reactions



M. Elder and B. R. Penfold, *Inorg. Chem.., 5, 1197(1966).*



Synthesis of Technetium Tetrachloride

Sealed tubes of technetium metal with excess chlorine gas (~ 1:6)

$$Tc + xs\ Cl_2 \rightarrow TcCl_4$$

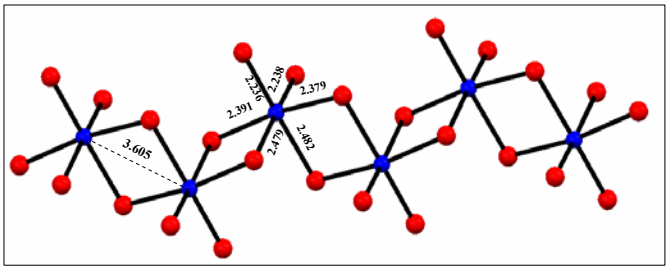
~ 20 mg of Tc metal

T= 450 °C, Cl_2 (g)

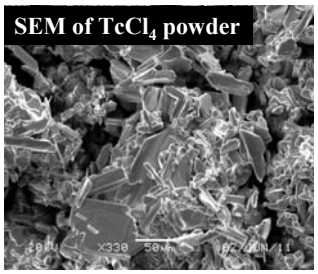
t = 14 hr,
~ 4.8 atm

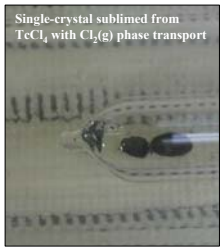
30-40 mg of $TcCl_4$ (~75% yield)

Technetium Tetrachloride



Endless chains of distorted edge-sharing $TcCl_6$ octahedra - orthorhombic *Pbca* space group

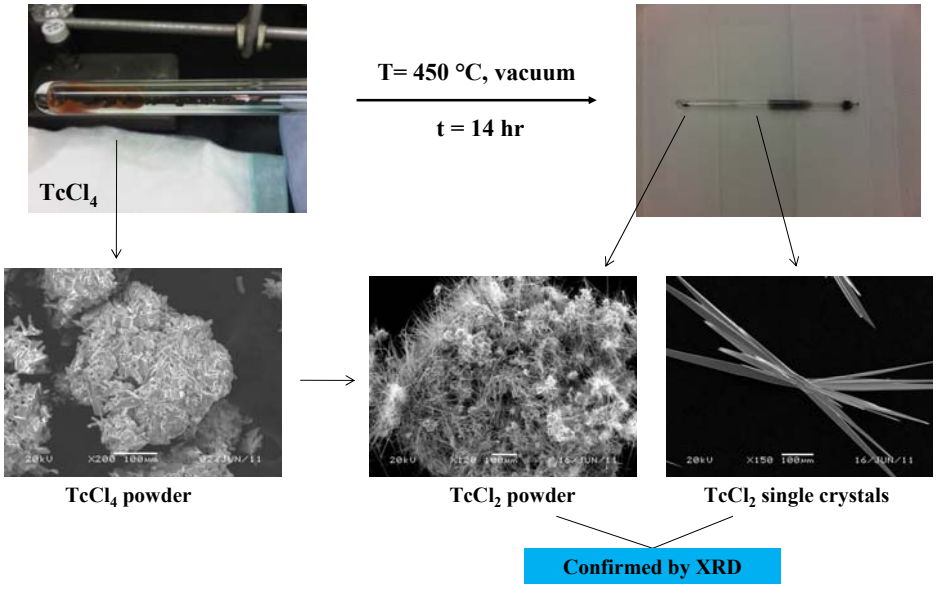




Unit Cell Comparison

	1965	1966	2011
a	11.58 Å	11.65 Å	11.531 Å
b	13.97 Å	14.06 Å	13.933 Å
c	5.98 Å	6.03 Å	6.011 Å

Decomposition of $TcCl_4$ to $TcCl_2$



Conclusions

- $TcCl_2$ was synthesized as a novel compound from the direct reaction of the elements, and was characterized by various techniques yielding a new structure for the transition metal binary halides containing metal-metal multiple bonds.

- A new, optimized synthetic method was determined for making $TcCl_4$ in sealed tube reactions with technetium metal and excess elemental chlorine, and the compound was characterized by various techniques

- Decomposition of $TcCl_4$ to $TcCl_2$ under vacuum yielded a new method for producing pure $TcCl_2$

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Contract No. 47824B Basic Energy Sciences, DOE
•Advanced Photon Source at Argonne National Laboratory

Questions?

7th International Symposium on Technetium and Rhenium Science and Utilization

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