Introduction to technetium chemistry

In Cooperation with our University Partners

Meet the Presenter… Dr. Frederic Poineau

Dr. Frederic Poineau is an Assistant Professor in the Radiochemistry Program at the University of Nevada Las Vegas. In 2001-2004, he performed his doctoral study at the laboratory Subatech (Nantes, France) on technetium chemistry. His thesis work focused on the speciation of tetravalent technetium complexes in chloride media. In 2005, he moved to UNLV where he conducted his post-doctoral researches. In 2016, he obtained his Habilitation from the University of Nantes. He is an expert on technetium chemistry, his research interests include: synthesis and coordination chemistry of technetium complexes with multiple metal-metal bonds, technetium binary materials (alloys, halides, oxides). He worked on the separation of uranium from technetium for the UREX process and on the development of Tc waste forms. He is regularly involved in the characterization of technetium, and f-elements compounds by diffraction and X-ray absoprtion fine structure spectroscopy. He has co-authored 96 articles, 2 book chapters and a patent.

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UNLV | RADIOCHEMISTRY PROGRAM

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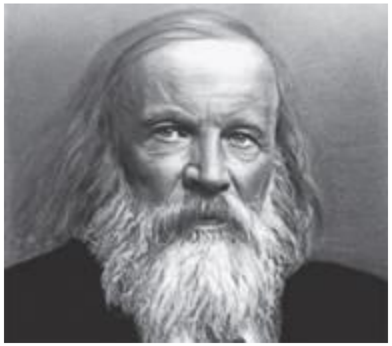
National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

TRAINING AND EDUCATION SUBCOMMITTEE

Element 43, Group 7- second row transition metal

❖1869: Predicted by D. Mendeleev



22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938 Manganese	26 Fe 55.845 Iron	27 Co 58.9332 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.4089 Zinc
40 Zr 91.224 Zirconium	41 Nb 92.9064 Niobium	42 Mo 85.94 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.9055 Rbodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.411 Cadmium
72 Hf 178.49 Hafnium	73 Ta 180.9497 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.217 Iridium	78 Pt 195.084 Platinum	79 Au 196.9666 Gold	80 Hg 200.59 Mercury

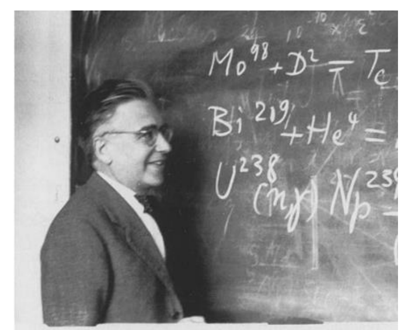
❖1934: Predicted to have no stable isotope (Mattauch rule)

❖1937: Discovered of Tc by E. Segre and C. Perrier

❖ 1938: Discovery of ^{99m}Tc by Segre and Seaborg

❖ 1952: Discovery of ^{99}Tc in a note from ORNL

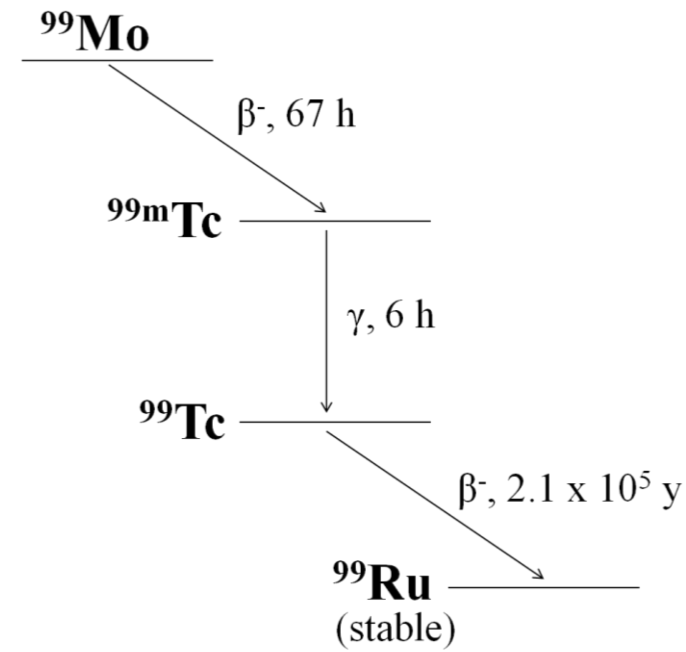
❖ 1961: Isolation of ^{99}Tc in pitchblende



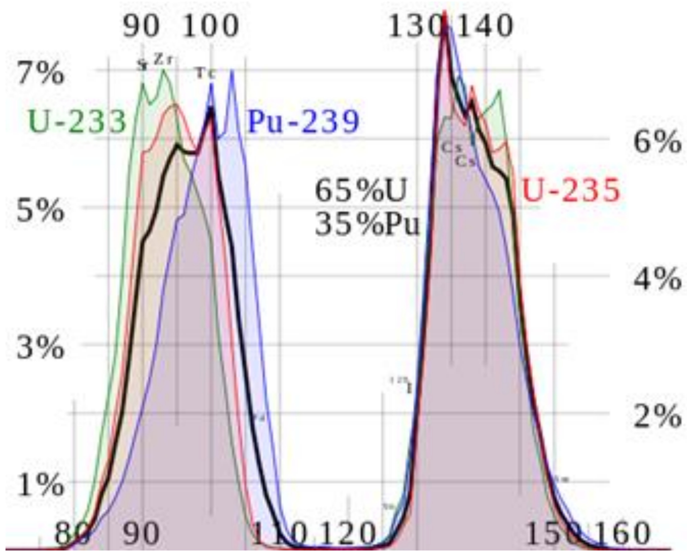
Lightest radioelement: 32 isotopes which are all radioactive

Longest lived isotopes: ^{97}Tc, ^{98}Tc and ^{99}Tc

Fission of ^{235}U →



Fission Yield (%)



Mass number

The isotope ^{99}Tc is a fission product, yield ~ 6 % from fission of ^{235}U

0.8 kg/MT of spent fuel (33 MWd/kg U)

Current Tc inventory in the US~ 56 MT (from spent fuel)

Present in small metallic inclusions as an alloy with Mo-Ru-Pd-Rh (ε-phases)

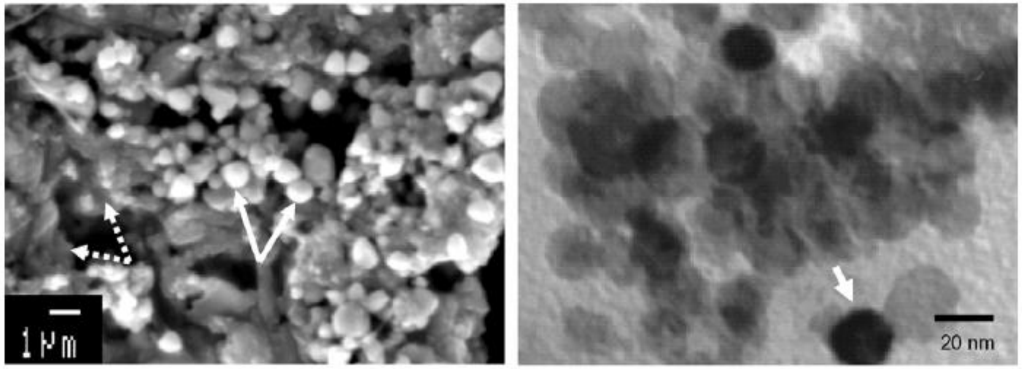
- **Composition (at %)**

Mo (30- 40), Ru (30-40), Tc (10), Pd (10-15), Rh (5)

- **Sizes: from 1 nm to 1 µm**

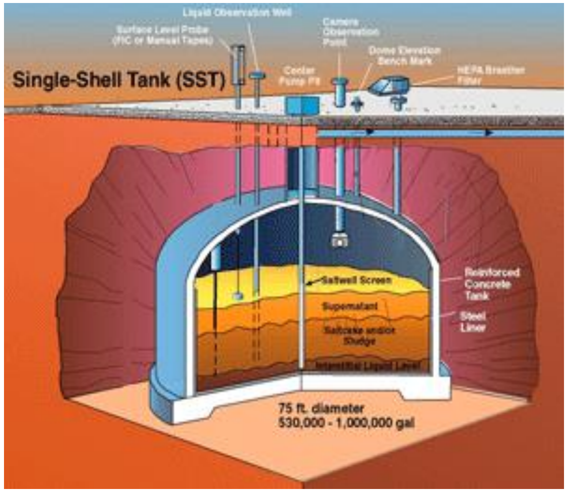
- **Very corrosion resistant**

Present in the dissolver during spent fuel reprocessing



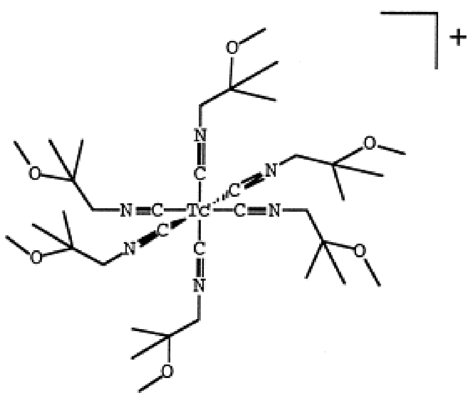
Technetium at the Hanford site

- Hanford (WA, US): primary site for production of plutonium for Manhattan Project
- Produced ~ 55 million gallons of radioactive waste which are stored in 177 tanks
- Approximately ~1500 kg of ^{99}Tc
  - Primarily present in the form of TcO_4^- (highly mobile)
- Separation of waste into high level (HLW) and low-activity (LAW) waste followed by vitrification
  - ^{99}Tc will be incorporated in the LAW glass and stored on site

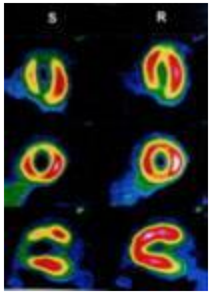


^{99m}Tc: Imaging agent in nuclear medicine ~90% of radio-diagnostic

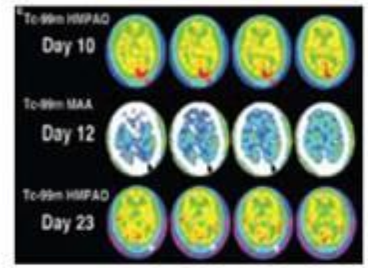
- **Optimal nuclear properties**: Energy allows imaging deep organ without damage
- **Versatile chemistry**: Coordination with suitable functional group (brain, heart, bone..)



Cardiolite: Heart imaging
40 million patients treated since 1991



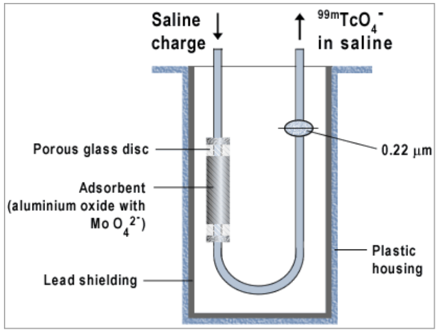
Heart



Brain

- **Available in ^{99}Mo/^{99m}Tc generator**

^{99}Mo: fission of highly enriched uranium in reactor



^{99}Mo/^{99m}Tc generator

Potential applications

Catalyst: Tc efficient catalytic properties for aldehyde production

Anti-corrosive agent: 55 ppm in steel avoids corrosion (passivation by insoluble Tc oxide). Tank in nuclear reactor.

Source of ruthenium (catalyst): transmutation of ^{99}Tc to ^{100}Ru

Transmutation of ^{99}Tc by neutron capture

$^{99}Tc + n \rightarrow {}^{100}Tc \rightarrow {}^{100}Ru$ (Stable) $+ \beta^-$

Exp. demonstration performed in 2003- 2008 in a fast neutron reactor

Phenix fast neutron reactor

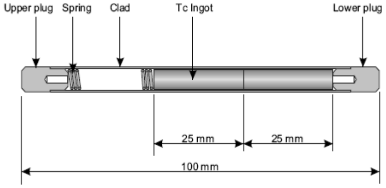


Figure 1. ANTICORP 1 pin drawings.

Assembly for transmutation

Transmuted Tc
Tc/Ru alloys

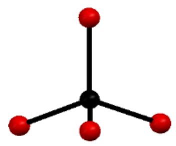
Five years irradiation: ~25 % of Tc transmuted into Ru

Technetium chemistry

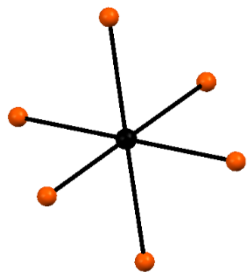
Electronic structure: [Kr]$4d^5 5s^2$, 9 oxidation states (+7 to -1)

Tc	4d config.	Compound
+7	d^0	$KTcO_4$
+6	d^1	$(TBA)TcNCl_4$
+5	d^2	$(TBA)TcOCl_4$
+4	d^3	K_2TcCl_6
+3	d^4	$(TBA)_2Tc_2Cl_8$
+2	d^5	$(TBA)Tc(NO)Cl_4$
+1	d^6	$K_5Tc(CN)_6$
0	d^7	$Tc_2(CO)_{10}$
-1	d^8	$[Tc(CO)_5]^-$

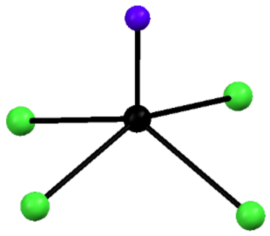
TBA: tetrabutyl-ammonium, $(Bu_4N)^+$



TcO_4^-



TcL_6 anion:
L = Cl, NCS, CN



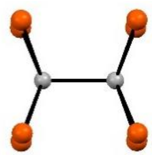
$TcLCl_4$ anion
L = N, O

Tc and Re share similar electronic structure

- ➢ Similar coordination complexes

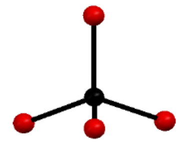
42 Mo 85.94 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium
74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium

Metal-metal bonded dimers



$M_2Cl_8^{2-}$

Heptavalent complexes



MO_4^-

➢Tc coordination chemistry less developed than Re

	Metal-metal bonded dimers	Heptavalent complexes
Tc	25	30
Re	500	150

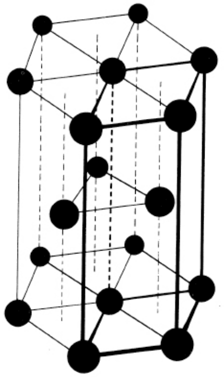
Understand fundamental chemistry of technetium

- ➢Development of new ^{99m}Tc imaging agents
- ➢Improve applications related to Hanford remediation
- ➢Improve applications related to management of spent fuel: waste form development
- ➢Predict behavior of Tc in environment

1. Introduction
2. Metal and binary compounds
3. Metal-metal bonded complexes
4. Aqueous solution chemistry
5. Summary

Metal

Structure: hexagonal compact (Hcp)
Density: 11.49
Melting point: 2200 °C
Boiling point: 4270 °C

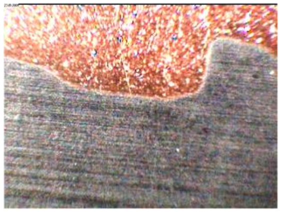


Preparation

→ Thermal reduction of NH_4TcO_4 under H_2 at T > 500 °C

$NH_4TcO_4 + 2H_2 \rightarrow Tc + 4H_2O + (1/2)N_2$

→ Electro-reduction of TcO_4^- in H_2SO_4



Tc metal on Cu electrode

Binary Oxides

Transition metal binary oxides: MO_n (n = 1- 4)
~70 are known (e.g., 5 for Mn, 3 for Re)

Two technetium binary oxides reported in the solid-state: TcO_2 and Tc_2O_7

Tc	Solid	Structure
+7	**Tc_2O_7**	Molecular dimer Similar to Mn_2O_7
+4	**TcO_2**	Extended structure Isostructural to ReO_2

Five binary oxides reported in the gas phases: TcO_3, Tc_2O_6, Tc_2O_5, Tc_2O_4, TcO

TcO_2

Decomposition of NH_4TcO_4 under Ar atmosphere at 750 °C

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

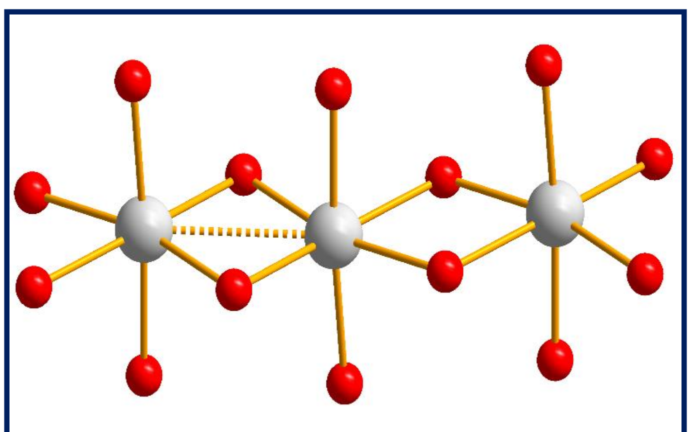
NH_4TcO_4

T = 750 ºC → Ar

TcO_2

Set-up

Extended structure: Characterization by NPD



Bond	Distance (Å)
Tc–Tc1	2.622(1)
Tc–Tc2	3.076(1)

- Tc-Tc bonding

TcO_2 is insoluble in H_2O (solubility: ~ 10^{-7}- 10^{-8} M)

Tc_2O_7

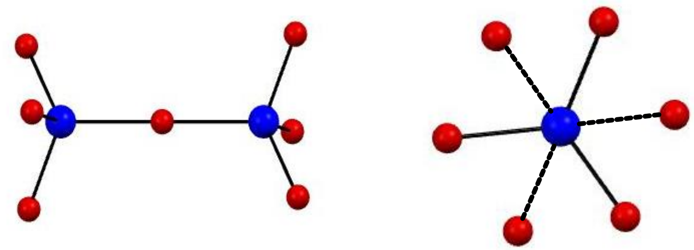
Oxidation of TcO_2 by O_2 at 450 °C in a sealed tube

- **$2\ TcO_2 + (3/2)O_2 \rightarrow Tc_2O_7$**

TcO_2

450 °C →
O2

Tc_2O_7



Molecular dimer

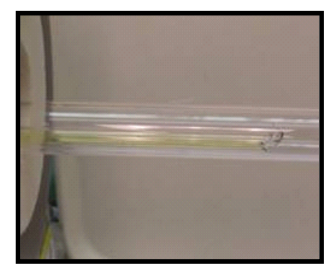
Properties

solid

120 °C →

liquid

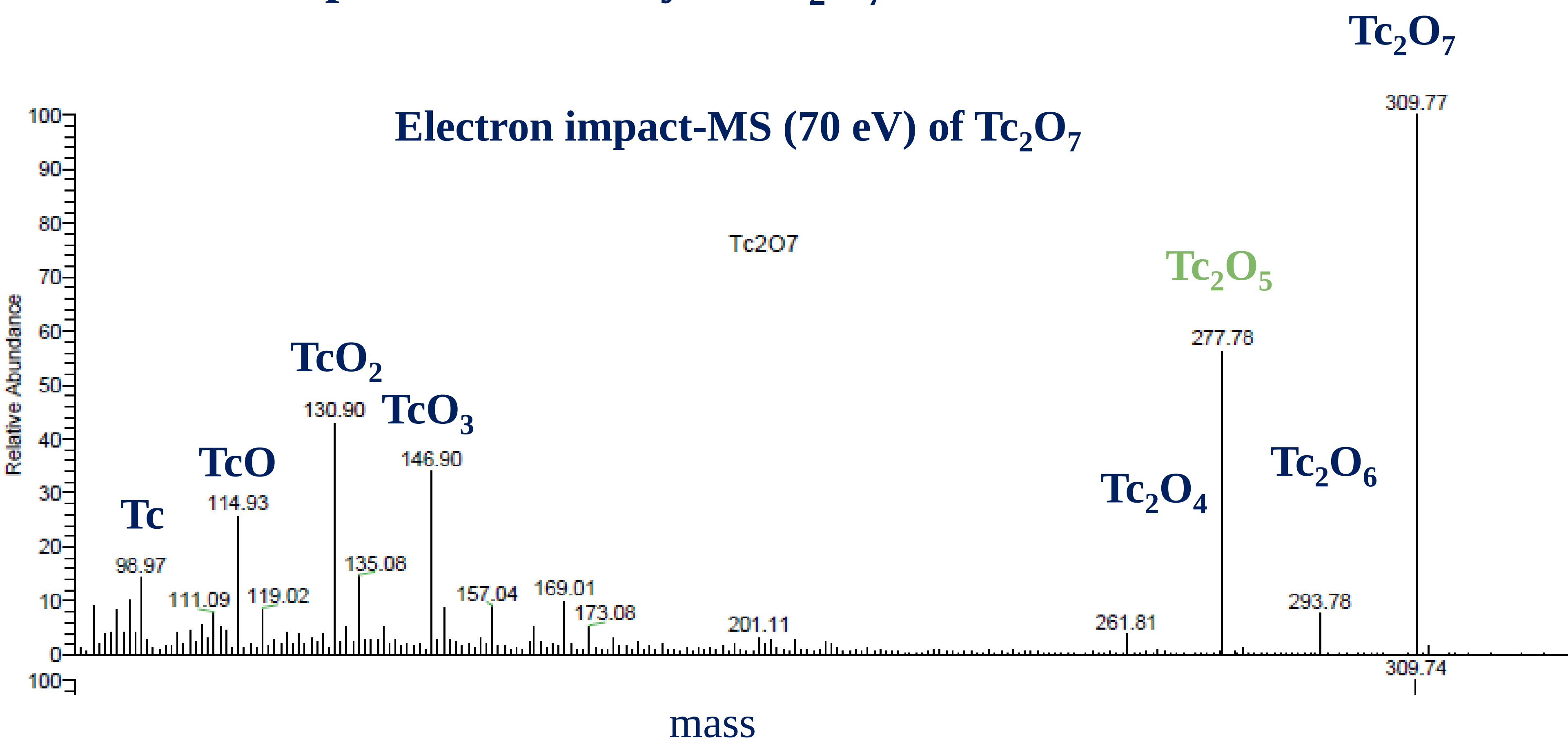
311 °C →



gas

Tc_2O_7 is highly volatile and soluble in H_2O

Gas phase chemistry of Tc_2O_7



Tc_2O_5: main fragmentation product of Tc_2O_7

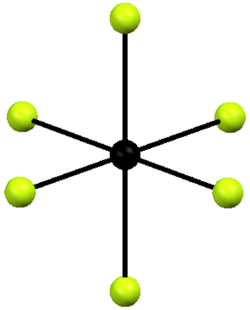
Binary Halides

Transition metal binary halides: MX_n (X = halide; n = 1-7)
~Two hundred are known (e.g., 13 for Mo, 14 for W and Re)
- **Ten Tc binary halides are known**

M	Fluorides	Chlorides	Bromides	Iodides
+2	-	α/β-$TcCl_2$	-	-
+3	-	α/β-$TcCl_3$ Re_3Cl_9	$TcBr_3$ Re_3Br_9	TcI_3 Re_3I_9
+4	- ReF_4	$TcCl_4$ $ReCl_4$	$TcBr_4$ $ReBr_4$	- ReI_4
+5	TcF_5 ReF_5	- $ReCl_5$	- $ReBr_5$	- -
+6	TcF_6 ReF_6	- $ReCl_6$	-	-
+7	ReF_7	-	-	-

Fluorides

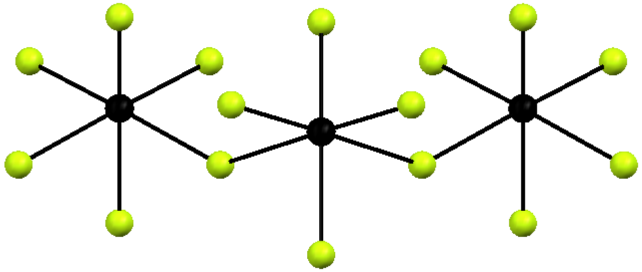
TcF_6 synthesized in 1961
$Tc + xs\ F_2 \rightarrow TcF_6$



Molecular TcF_6

Tc(+6), d^1
Isostructural to ReF_6

TcF_5 synthesized in 1963
$Tc + xs\ N_2/F_2 \rightarrow TcF_5$



Chain of corner sharing TcF_6 octahedra

Tc(+5), d^2
Isostructural to ReF_5

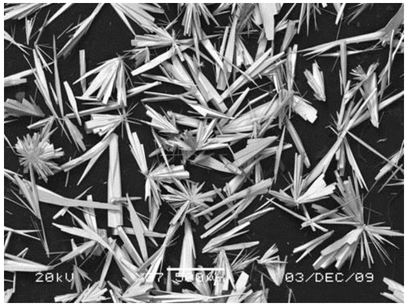
Chlorides

Reaction between Tc metal and Cl_2 in sealed tube (Tc:Cl ~ 1:2)

24 h, 450 °C

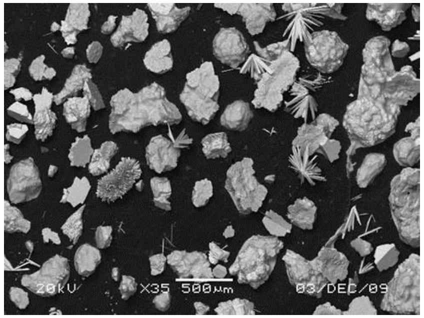
Needles + metal

β-$TcCl_2$ + Tc metal



Needles

β-$TcCl_2$

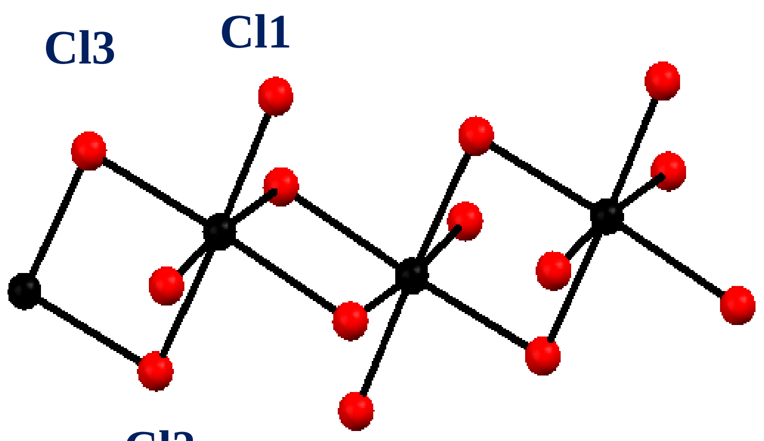


Dark-red film

$TcCl_4$ + β-$TcCl_3$

Technetium tetrachloride

Technetium tetrachloride synthesized in 1957



$Tc + xs\ Cl_2 \rightarrow TcCl_4$

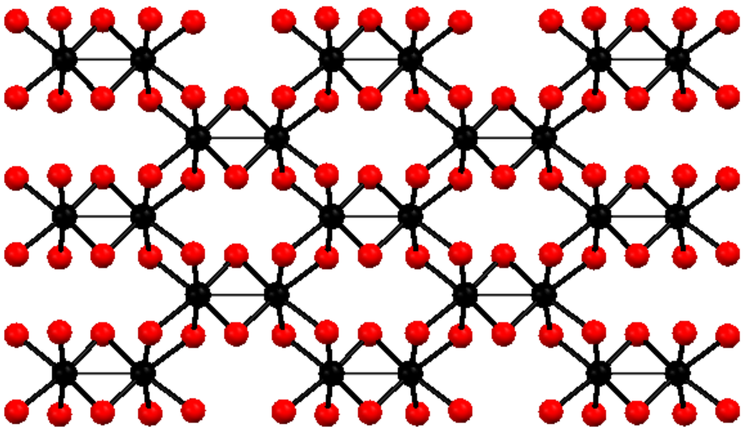
Infinite chain of edge-sharing $TcCl_6$ octahedra

Tc···Tc	3.62	Tc-Cl3	2.38
Tc-Cl1	2.25	Tc-Cl2	2.49

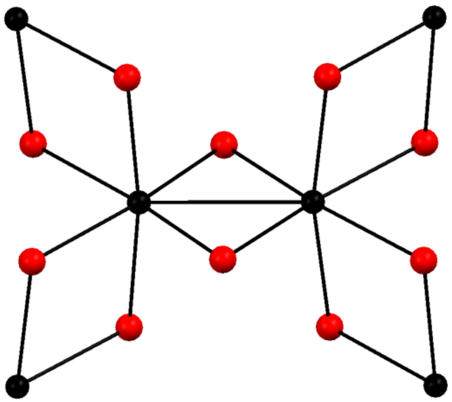
- Tc…Tc = 3.62 Å: no Tc-Tc bond
- $TcCl_4$ is paramagnetic (d[3] configuration)
- Precursor for synthesis, $TcCl_4L_2$; L= THF, H_2O

β-Technetium trichloride

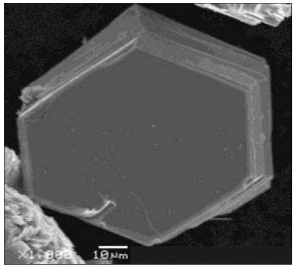
β-$TcCl_3$: Infinite layers of edge -sharing $TcCl_6$ octahedra



β-$TcCl_3$ layer



$[Tc_2Cl_{10}]$ unit in β-$TcCl_3$



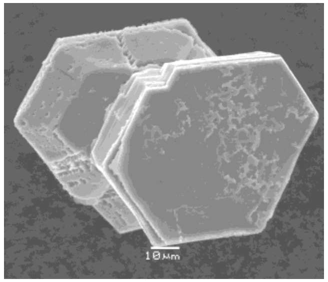
β-$TcCl_3$

Tc
Cl

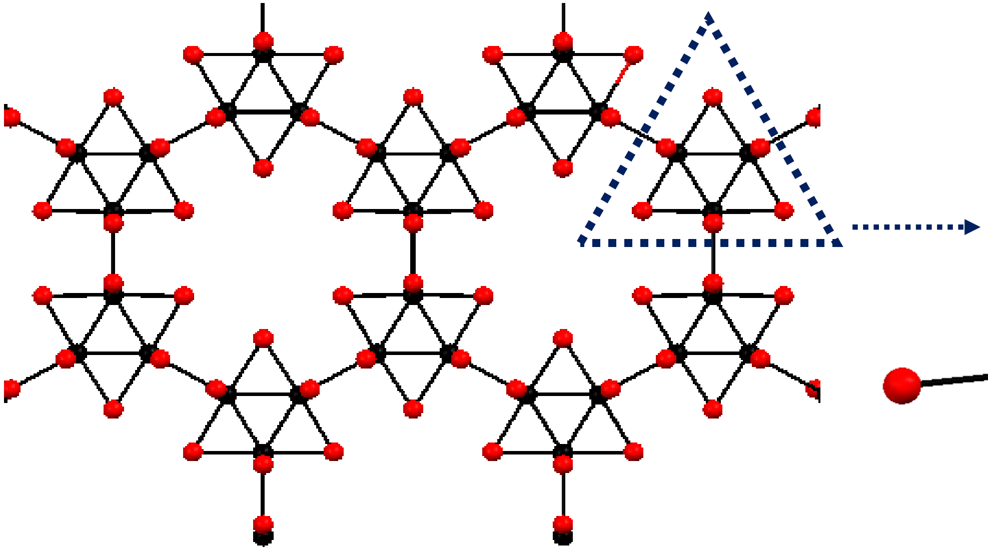
- **β-$TcCl_3$ crystallize with the "$MoCl_3$" structure-type**
- **Tc-Tc = 2.861(1) Å, presence of Tc=Tc double bond**
- **β-$TcCl_3$ converted to α-$TcCl_3$ at 280 °C in 10 days**

α-Technetium trichloride

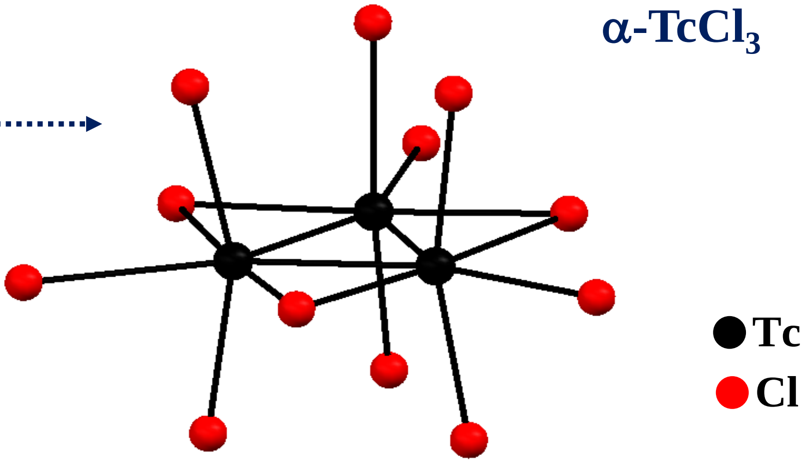
α-$TcCl_3$: Infinite layers of Tc_3Cl_9 bridged by Cl ligands



α-$TcCl_3$



α-$TcCl_3$ layer



Tc_3Cl_9 cluster in α-$TcCl_3$

- **α-$TcCl_3$ crystallize with the "$ReCl_3$" structure-type**
- **Tc-Tc separation of 2.444(1) Å**
- **Presence of Tc=Tc double bonds**

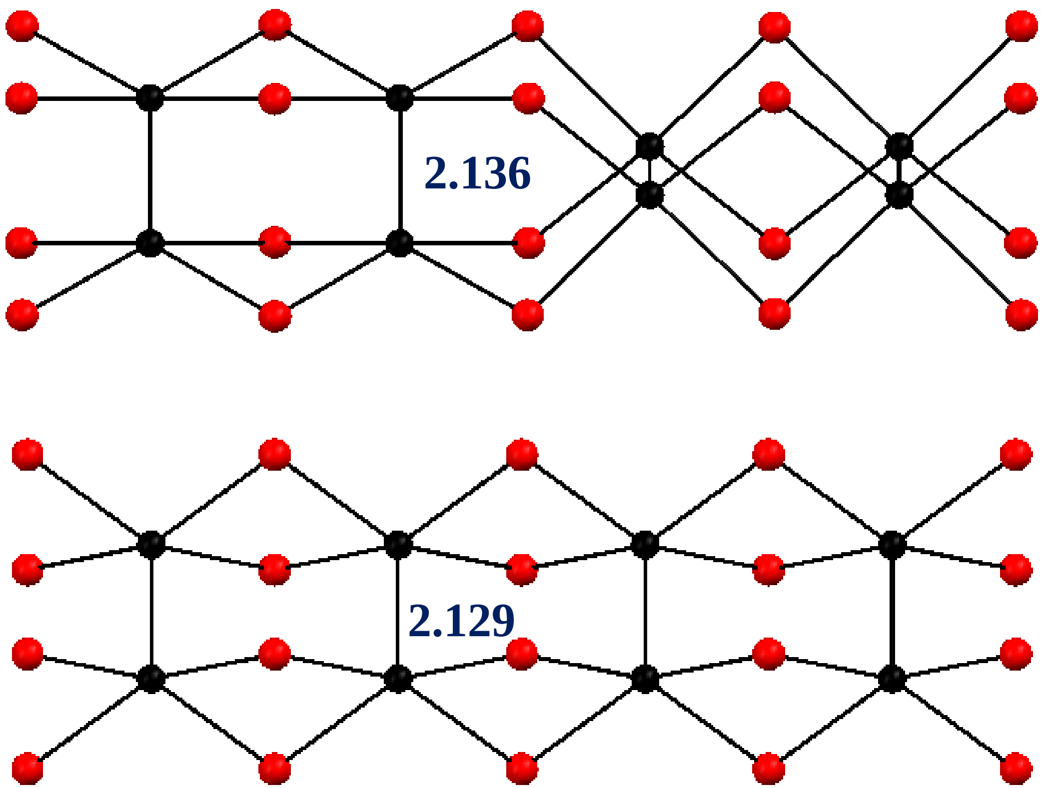
Technetium dichloride

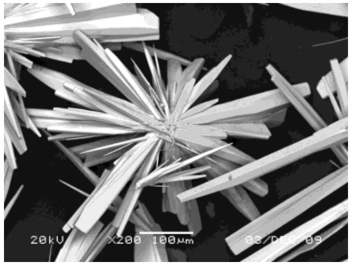
β-$TcCl_2$: Infinite chains of face-sharing Tc_2Cl_8 rectangular prisms

β-$TcCl_2$

$AlCl_3$ ↓ 450 °C

α-$TcCl_2$





β-$TcCl_2$

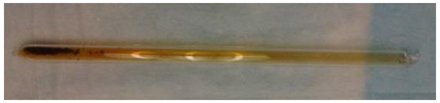
● Tc
● Cl

- ➢ β -$TcCl_2$: new structure-type
- ➢ Tc-Tc separation of 2.136(1) Å (Tc≡Tc triple bond)
- ➢ β-$TcCl_2$ converted to α-$TcCl_2$ at 450 °C with $AlCl_3$

Bromides

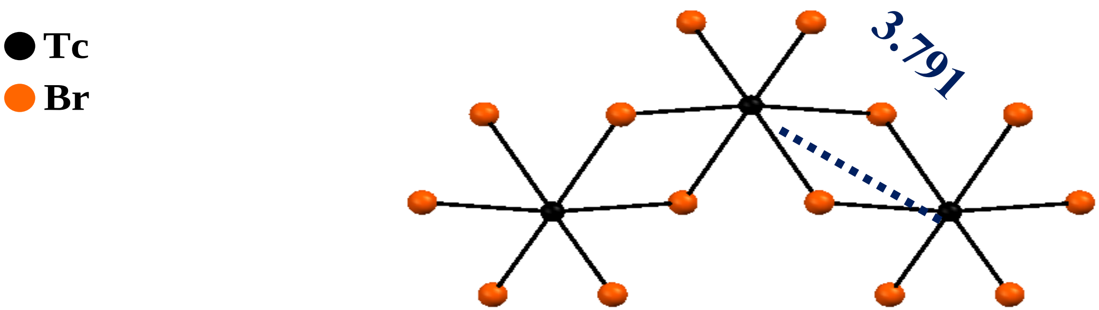
Technetium tetrabromide

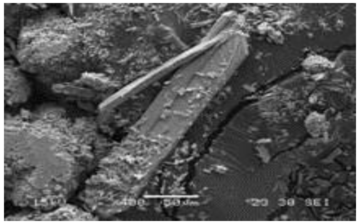
Reaction between Tc metal and Br_2 in sealed tube (Tc:Br ~ 1:4)



400 °C

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





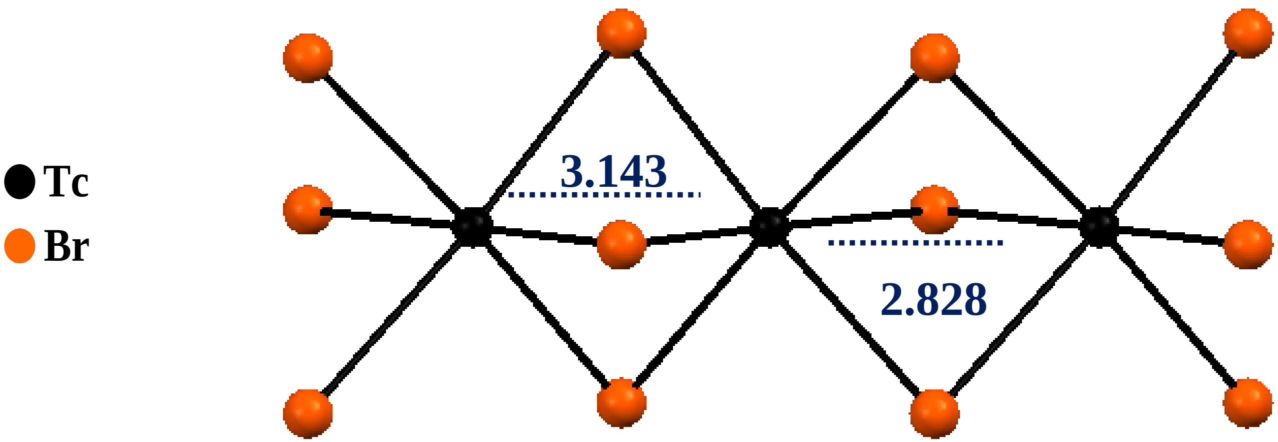
$TcBr_4$

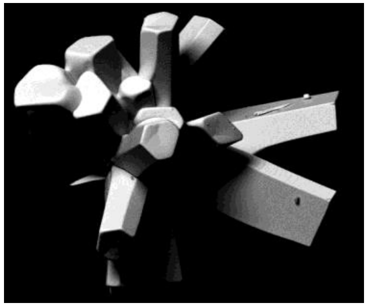
- **Only group 7 binary tetrabromide characterized**
- **Crystallizes in the $TcCl_4$ structure-type**
- **Tc-Tc = 3.791 Å; absence of metal-metal bond**

Technetium tribromide

Reaction between Tc metal and Br_2 in sealed tube (Tc:Br ~ 1:3)

$TcBr_3$: Infinite chains of face-sharing $TcBr_6$ octahedra





$TcBr_3$

- $TcBr_3$ is isostructural to $MoBr_3$ and $RuBr_3$
- Alternation short (2.828(1) Å) /long (3.143(1) Å) Tc-Tc separation
- Presence of Tc=Tc bond

Iodide

Technetium triiodide

Reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and HI gas

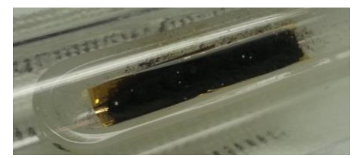
TcI_3: infinite chains of face-sharing TcI_6 octahedra

$Tc_2(O_2CCH_3)_4Cl_2$

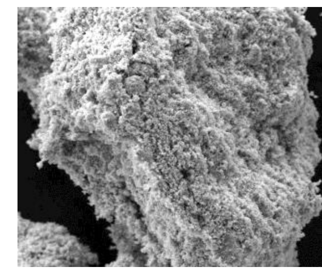
150 °C

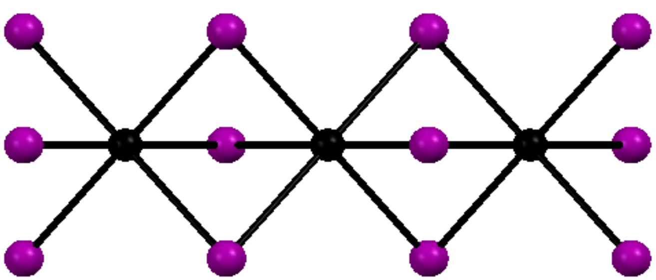
→

HI g



TcI_3





- **Only Tc binary iodide reported**
- **Tc…Tc = 3.10 and 2.67 Å**
- **Isostructural to MoI_3 and RuI_3**

Binary Carbides

Reaction between Tc metal and graphite at 1050 °C
Nature of reaction product depends on Tc:C ratio

- **For C< 1%: solid-solution of carbon in Tc metal**
- **For 1 <C< 9%: new phase →TcC**
  - ➢**Structure not reported**

Binary Nitrides

Tc nitride formed by thermal decomposition of $[NH_4]_2TcCl_6$ under N_2

➢**Stoichiometry : $TcN_{0.75}$.**

➢ **Structure unknown**

$[NH_4]_2TcCl_6$

300 °C → **N_2**

$TcN_{0.75}$

Binary Sulfides

Two sulfides reported: Tc_2S_7 and TcS_2

Tc_2S_7: reaction between TcO_4^- and H_2S in acidic solution

- **X-ray structure unknown**

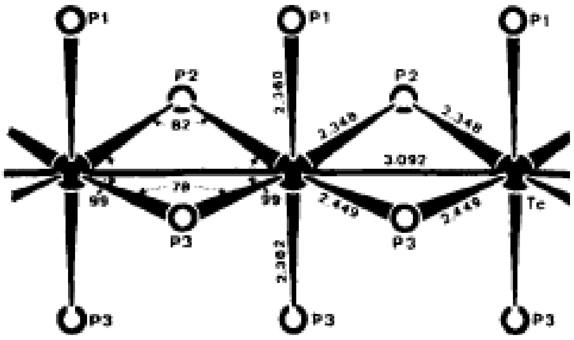
TcS_2: decomposition of Tc_2S_7 at 1000 °C or reaction between Tc metal and S in a sealed tube at 450 °C

- **Isostructural to ReS_2**

Binary Phosphides

Reaction between Tc metal and phosphorous in a sealed tube (1000 °C)

- **Four binary phosphides: Tc_3P, Tc_2P_3, TcP_3 and TcP_4**



TcP_3: edge sharing TcP_6 octahedron

1. Introduction
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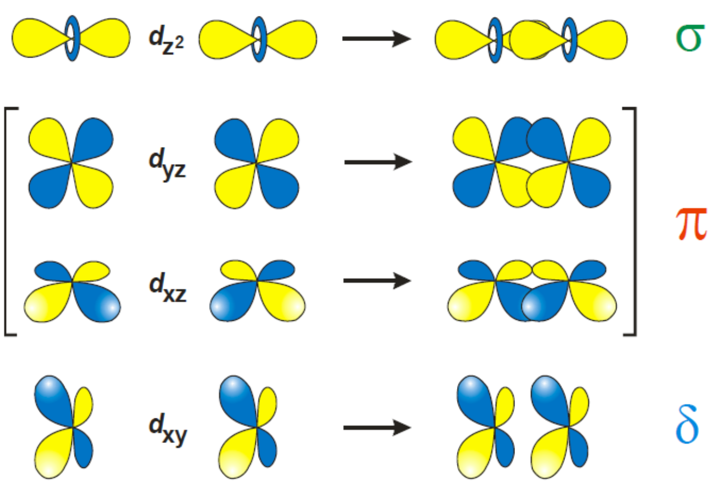
Tc has high tendency to form metal-metal bonds in low oxidation state

Concept of multiple metal-metal bond introduced in 1964 for $Re_2Cl_8^{2-}$

Metal-metal bonded dimers: M_2^{n+} units coordinated to ligands

In the M_2^{n+}: d orbitals can overlap and form σ, π and δ bonds

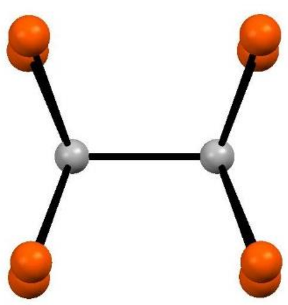
Technetium: Tc_2^{6+}, Tc_2^{5+} and Tc_2^{4+} unit



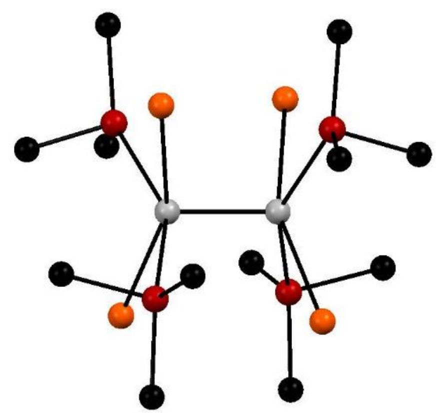
- **500 Re and 30 Tc complexes with multiple M-M bonds reported**

Complexes with multiple Tc-Tc bonds reported for Tc in the +3, +2, and +1 oxidation state

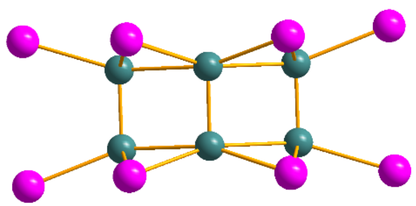
(Tc;Tc)	Complex	Bond multiplicity	
(+3;+3)	$(TBA)_2Tc_2Cl_8$	[Tc≣Tc]	Quadruple bond
(+3;+2)	$Cs_3Tc_2Br_8$	[Tc≡Tc]	Triple bond
(+2;+2)	$Tc_2Br_4(PMe_3)_4$	[Tc≡Tc]	Triple bond
(+1;+2)	Tc_8I_{12}	[Tc-Tc] [Tc≣Tc]	Single and quadruple bond



$Tc_2X_8^{n-}$



$Tc_2X_4(PMe_3)_4$



Tc_8I_{12} cluster

Preparation of $Tc_2Cl_8^{2-}$

Successive reductions: Tc(VII) →Tc(V) → Tc(III)

TcO_2/NH_4TcO_4

NH_4OH, H_2O_2

→

(*TBA*)HSO_4

(*TBA*)$Tc^{VII}O_4$

12 M HCl

→

T = 0 °C

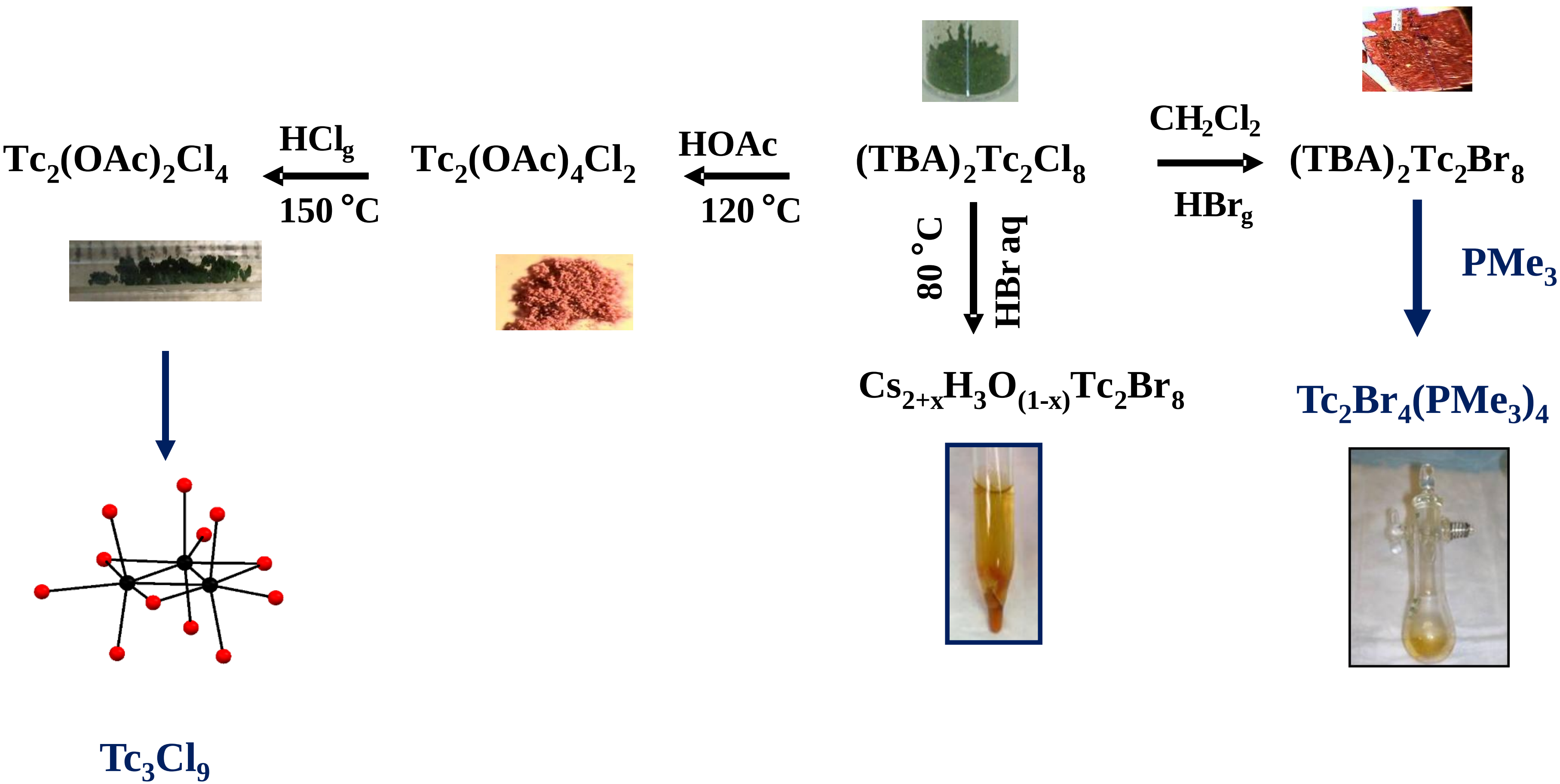
(*TBA*)$Tc^{V}OCl_4$

↓

(*n*-Bu_4N)BH_4
THF
&
HCl,
acetone

(*TBA*)$_2Tc^{III}{}_2Cl_8$

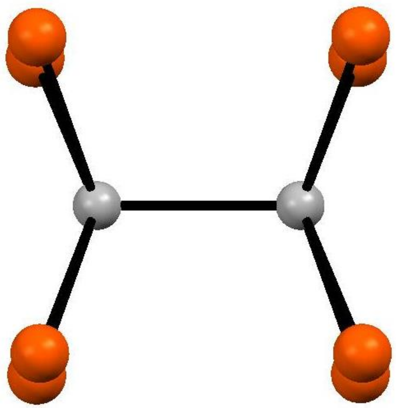
Preparation of dimers with Tc_2^{6+},Tc_2^{5+} and Tc_2^{4+} units



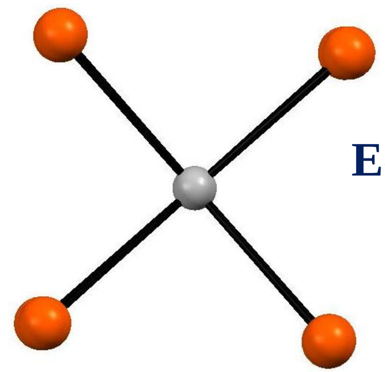
Reaction mechanisms from $(TBA)_2Tc_2Cl_8$ to Tc_3Cl_9 mimic the one of Rhenium

$Tc_2X_8^{2-}$

Crystallization from acetone / ether for single crystal XRD
→ Formation of an acetone solvate: $(TBA)_2Tc_2X_8 \cdot 4[(CH_3)_2CO]$



$Tc_2X_8^{2-}$



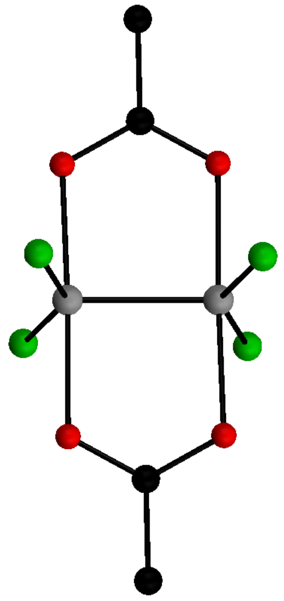
Eclipsed $TcCl_4$ units

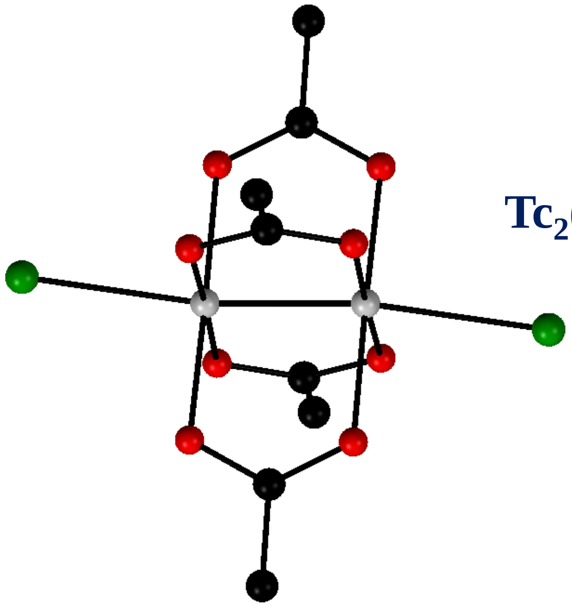
Anions	Tc-Tc (Å)	<Tc-Tc-X> (°)
$Tc_2Br_8^{2-}$	2.1625(9)	105.01(3)
$Tc_2Cl_8^{2-}$	2.1560(3)	103.92(2)

Steric effect induced by bromide in $Tc_2Br_8^{2-}$ ion
Increase of Tc-Tc separation and Tc-Tc-X angle

$Tc_2(O_2CCH_3)_2Cl_4$ and $Tc_2(O_2CCH_3)_2Cl_4$

$Tc_2(OAc)_2Cl_4$





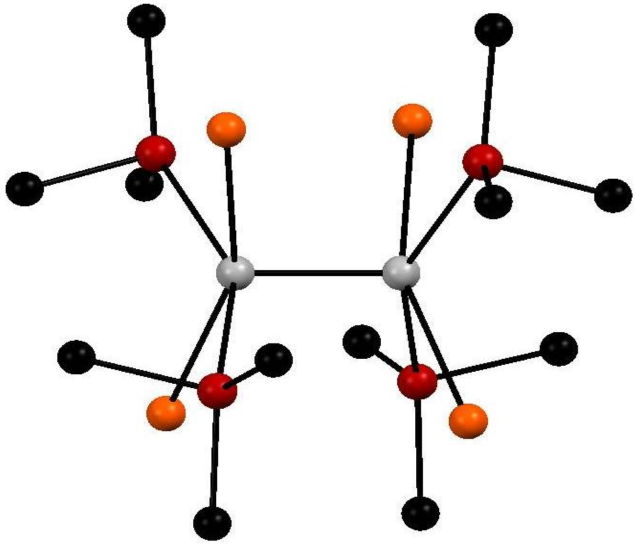
$Tc_2(OAc)_4Cl_2$

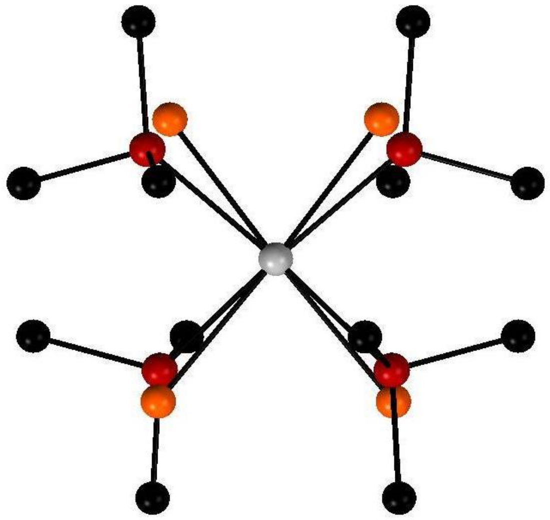
Compounds	Tc-Tc (Å)	Tc-X (Å)
$Tc_2(O_2CCH_3)_4Cl_2$	2.176(1)	2.508(4)
$Tc_2(O_2CCH_3)_2Cl_4$	2.150(1)	2.312

Decrease of Tc-Tc from $Tc_2(O_2CCH_3)_4Cl_2$ to $Tc_2(O_2CCH_3)_2Cl_4$

Influence of axial Cl ligand on Tc-Tc separation

$Tc_2X_4(PMe_3)_4$



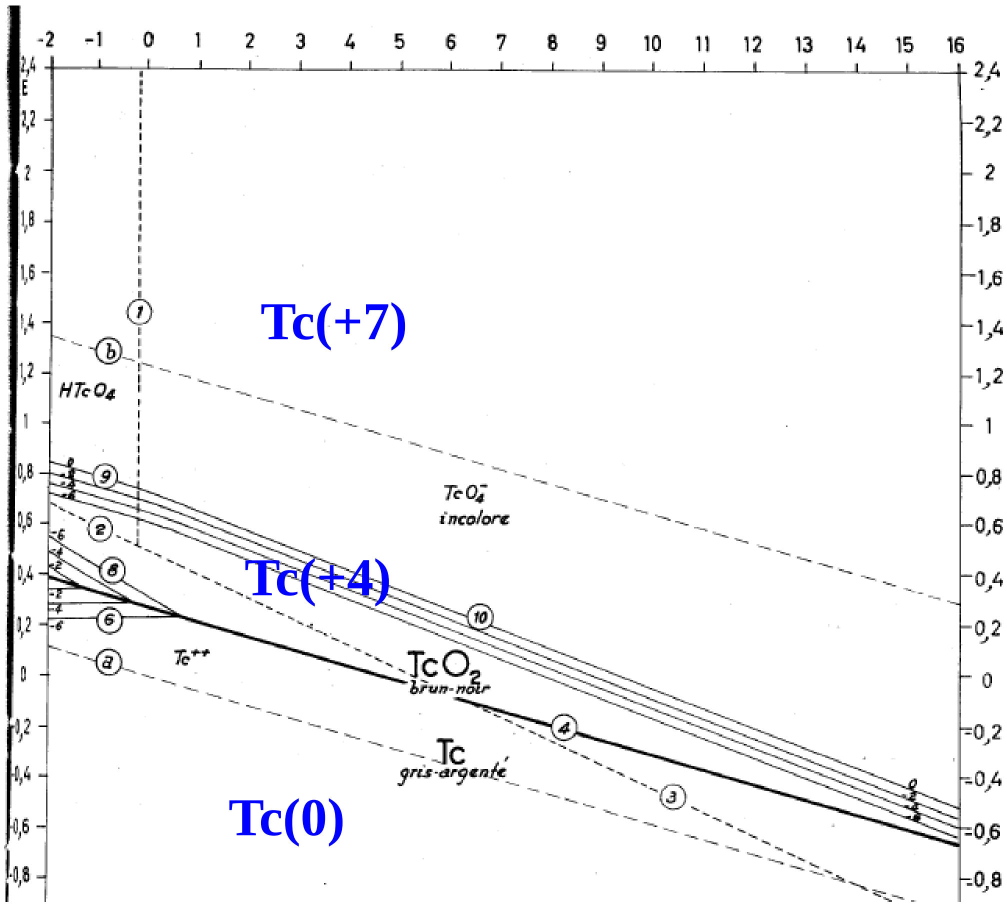


compound	Average distances (Å)		
	Tc-Tc	Tc-X	Tc-P
$Tc_2Br_4(PMe_3)_4$	2.1316(5)	2.520[1]	2.441[1]
$Tc_2Cl_4(PMe_3)_4$	2.1318(3)	2.3858[5]	2.4356[4]

Tc_2^{4+} is not sensitive to the nature of coordinating halide

Non-complexing media

Speciation depends on Eh and pH of the solution



➢Three oxidation states are thermodynamically stable Tc(+7), Tc(+4) and Tc(0)

In aqueous oxidizing media: Tc speciation dominated by Tc(+7)

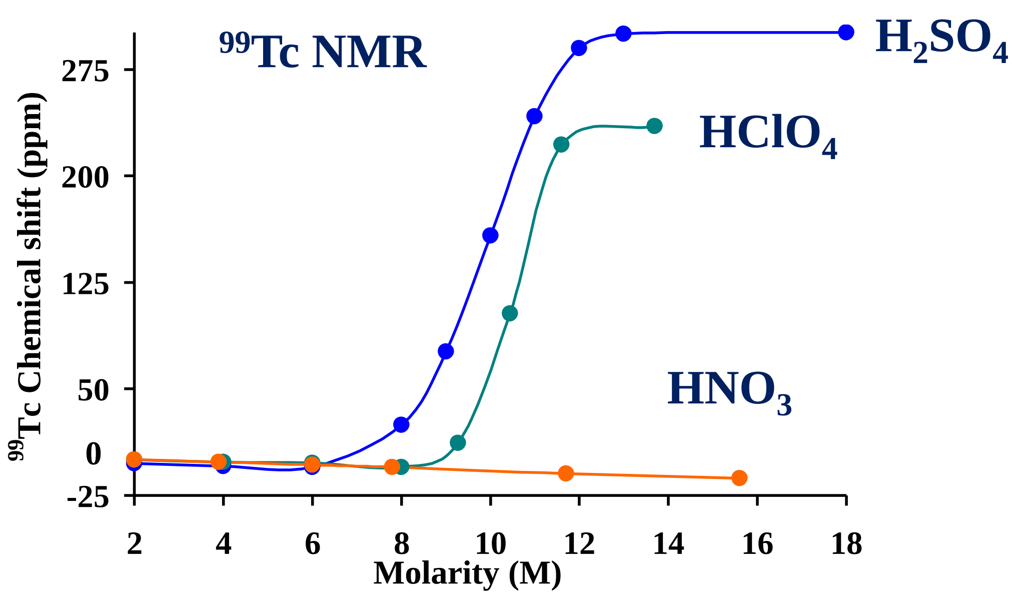
➢ TcO_4^- (well characterized) and $HTcO_4$ (poorly studied)

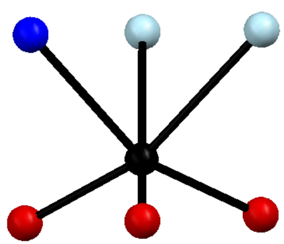
Speciation of Tc(+7) in HNO_3, H_2SO_4 and $HClO_4$

Dissolution of $KTcO_4$ in $HClO_4$, H_2SO_4 and HNO_3

For [1 -15.6 M] HNO_3: colorless solutions→ TcO_4^-

For $HClO_4$ and H_2SO_4 > 8 M: yellow solutions→ $TcO_3OH(H_2O)_2$





$TcO_3(OH)(H_2O)_2$

Tc(+6), Tc(+5), Tc(+3) are thermodynamically unstable

→ Disproportionation

Tc	Media	Reaction
+6	Basic	2Tc(+6) →Tc(+7) + Tc(+5)
+5	neutral	3Tc(+5) → Tc(+7) + 2Tc(+4)
+3	Acid	5Tc(+3) → 4Tc(+4) + Tc(0)

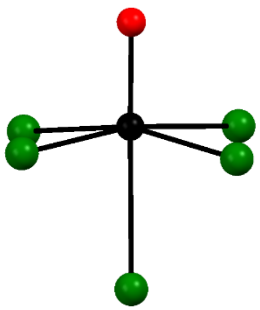
Complexing media

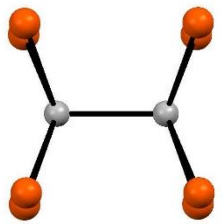
Chloride media

Four chloro- species identified in concentrated HCl

Tc	Media	Species
+6	HCl/H_2SO_4	$TcOCl_5^-$
+5	Cold HCl	$TcOCl_5^{2-}$
+4	Warm HCl	$TcCl_6^{2-}$
+2, +3	Warm HCl + Zn powder	$Tc_2Cl_8^{3-}$

$TcOCl_5^-$





$Tc_2Cl_8^{3-}$

TcO_4^- is unstable in 12 M HCl: reduction of Tc by Cl-

Cold HCl **Cold HCl** **Warm HCl**

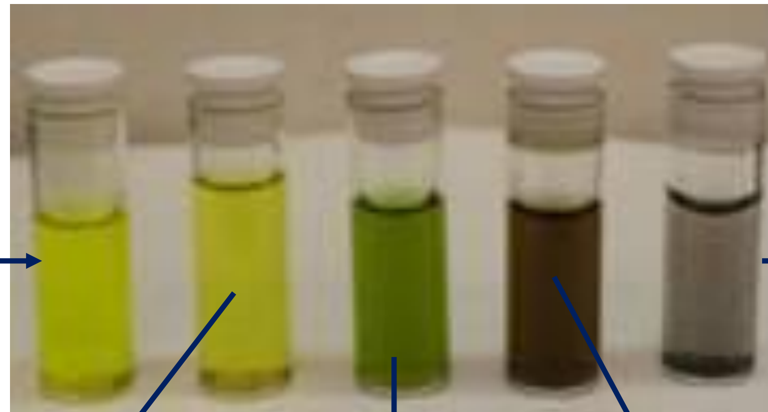
$TcO_4^- \rightarrow TcOCl_5^- \rightarrow TcOCl_5^{2-} \rightarrow TcCl_6^{2-}$

Further reduction of Tc(IV) in warm HCl by Zn

$TcCl_6^{2-} + Zn \rightarrow Tc_2Cl_8^{3-} + Zn^{2+}$

$TcCl_6^{2-}$ is unstable below 1 M HCl and hydrolyses

pH 0 0.1 0.3 1 4



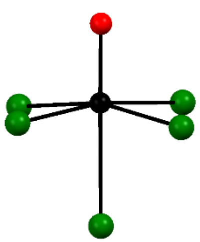
$TcCl_6^{2-}$

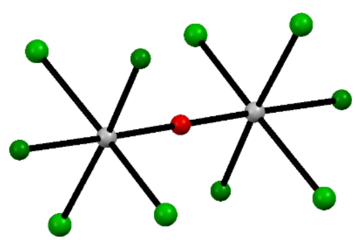
$TcO_2.xH_2O$

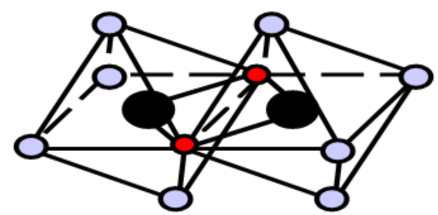
$TcCl_5(H_2O)^-$

$Tc_2OCl_{10}^{4-}$

$Tc_nO_y^{(4n-2y)+}$







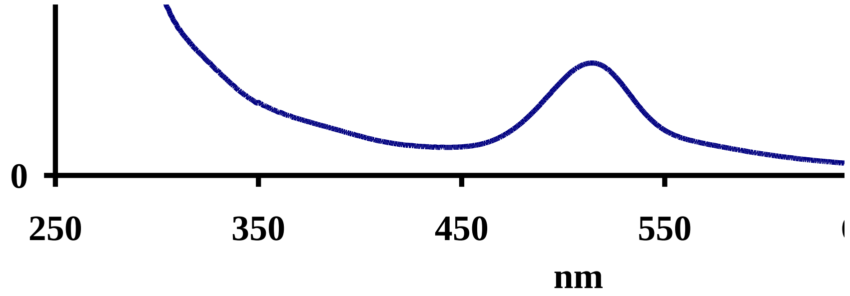
Carbonate media

Tc(IV) and Tc(III) complexes reported in carbonate solution

Tc(IV): electro-reduction of TcO_4^-, dissolution of TcO_2 or $[NH_4]_2TcCl_6$

- **Characterized by UV-Visible spectroscopy**
  - **Structure unknown: monomeric or polymeric ?**

Tc(IV) in 2 M $KHCO_3$



Tc	Solution	Stoichiometry
+4	pH = 7.3 HCO_3^- = 0.5 M Electro-reduction	$Tc(CO_3)_q(OH)_n^{(4-n-2q)+}$?
+3		$Tc(CO_3)_q(OH)_n^{(3-n-2q)+}$?

No Tc carbonate solid reported

1. Introduction
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Group VII second row transition metal
Predicted 150 years ago and discovered 80 years ago

Lightest radioactive element (no stable isotopes)
Two isotopes of interest
^{99}Tc (β^-): fission product of nuclear industry (6% yield from ^{235}U)
Inventory : 56 MT from spent fuel and 1.5 MT at the Hanford site
^{99m}Tc(γ): produced from ^{99}Mo decay, imaging agent: cardiolite 40 million treated

Inorganic chemistry
Rich redox- chemistry with 9 oxidations states
Chemistry similar to Re (especially in +4 and +7 states, i.e., binary oxides)
Solid-state compounds: rich and unique halides chemistry (i.e., $TcCl_2$ structure-type)
Lack of data for nitrides, sulfides and carbides materials
High tendency to form multiple metal-metal bond in low valent states (i.e., $Tc_2X_8^{n-}$)

Aqueous chemistry
Non complexing: 3 oxidation states are thermodynamically stable (+7, +4 and 0)
Con. HCl; Tc(+6), Tc(+5), Tc(+4) and Tc(+2.5) complexes characterized
Carbonate: Tc(+4) and Tc(+3) reported but not characterized

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UNLV Radiochemistry Program

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