Technetium Binary Halides:
from Molecular to Extended Structures

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Technetium Chemistry at UNLV

Fundamental and Applied Research on Technetium

Synthetic, coordination and computational chemistry
- Metal-metal bonded dimer, binary halides, oxides.

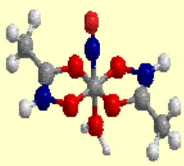
$Tc_2Cl_4(PMe_3)_4$

Chemistry relevant to the nuclear fuel cycle
-Separations and development of technetium waste forms
-Corrosion metallic technetium and alloys

U/Tc separation

Chemistry relevant to radiopharmaceuticals
- ^{99}Tc nitrosyl and phosphine complexes

Better understand fundamental chemistry
→ New applications (waste form, separations…)



$Tc(NO)(AHA)_2(H_2O)^+$

Fundamental Tc chemistry

Study of Tc complexes with quadruple metal-metal bond and their transformation to binary halides

Background

I. Studies of the precursors: the quadruply bonded Tc dimers

A - $(n\text{-}Bu_4N)_2Tc_2Br_8$
B - $Tc_2(O_2CCH_3)_4X_2$ (X = Cl, Br)
C - $Tc_2(O_2CCH_3)_2Cl_4$

II. Synthesis and characterization of Tc binary halides

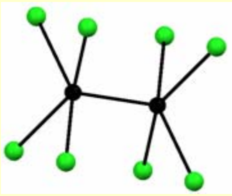
A - Technetium trichloride
B - Technetium tribromide
C - Binary halides as precursors of low-valent complexes

Conclusions

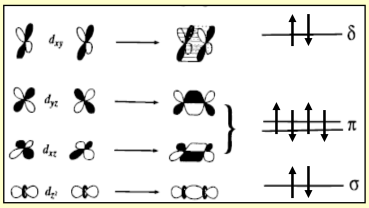
Background

Quadruply metal-metal bonded dimers

- Complexes which exhibit four bonds (1 σ, 2 π and 1 δ) between metal centers



Quadruple bond identified in 1964 in $Re_2Cl_8^{2-}$



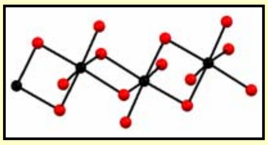
AOs involved in quadruple bond

- Known for group VI and VII; ~ 300 for Mo and ~100 for Re
- Five Tc quadruple bonded dimers structurally characterized: $(n\text{-}Bu_4N)_2Tc_2Cl_8$, $Tc_2(O_2CCMe_3)_4Cl_2$, $Tc_2(O_2CMe)_4(TcO_4)_2$, $Tc_2(O_2CCH_3)_2Cl_4$▪2dma and $K_2Tc_2(SO_4)_4$▪$2H_2O$

- **No bromides or iodides have been structurally characterized $(n\text{-}Bu_4N)_2Tc_2Br_8$ and $Tc_2(O_2CCH_3)_4X_2$ (X = Cl, Br) previously reported, but not well characterized**

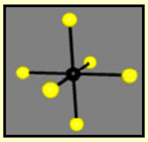
Transition metal binary halides

- MX_n (X = halide, and n = 1-7)
- Two hundred are known (e.g., 13 for Re and Mo, 14 for W)
- Formed by reaction between metal and element or between molecular complexes and HX (X = Cl, Br, I) gas
- Only three technetium binary halides: $TcCl_4$, TcF_6 and TcF_5



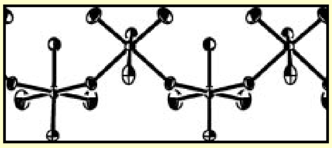
$TcCl_4$: in 1957

$Tc + xs\ Cl_2 \rightarrow TcCl_4$



TcF_6: in 1961

$Tc + xs\ F_2 \rightarrow TcF_6$



TcF_5: in 1963

$Tc + xs\ N_2/F_2 \rightarrow TcF_5$

- **No binary iodides and bromides known**
- **No trivalent or divalent Tc binary halides reported**
- **No reaction involving molecular complexes and HX gas reported**

GOAL

Explore the coordination and synthetic chemistry of Tc binary halides and quadruple metal-metal bonded dimers:

- **Structure and bonding of $Tc_2Br_8^{2-}$ and $Tc_2(O_2CCH_3)_4X_2$ (X = Cl, Br)**
- **Synthesis of binary halide from reaction $Tc_2(O_2CCH_3)_4Cl_2$ and HXg (X= Cl, Br)**
- **Study of structure of Tc binary halides and comparison with Re, Mo, Ru**
- **Binary halides as precursor for synthesis of new complexes**

I. Studies of the precursors: the quadruply-bonded Tc dimers

A - $(n\text{-}Bu_4N)_2Tc_2Br_8$

Preparation

TcO_2/NH_4TcO_4

T = 100 °C, H_2O_2

$(n\text{-}Bu_4N)OH$

$(n\text{-}Bu_4N)TcO_4$

12 M HCl

T = 0 °C

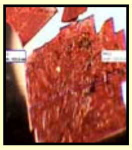
$(n\text{-}Bu_4N)TcOCl_4$

$(n\text{-}Bu_4N)BH_4$
THF
&
HCl,
acetone

$(n\text{-}Bu_4N)_2Tc_2Cl_8$

HBr_{gas}

T = 30 °C

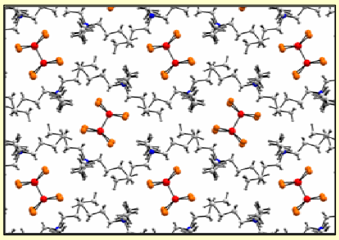


$(n\text{-}Bu_4N)_2Tc_2Br_8$

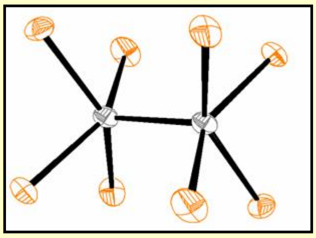
Single-crystal XRD

Recrystallization from acetone/ether provides single crystals

→ Formation of an acetone solvate: $(n\text{-}Bu_4N)_2Tc_2Br_8.\ 4[(CH_3)_2CO]$*



View of the solvate from the a direction



$Tc_2Br_8^{2-}$ ion

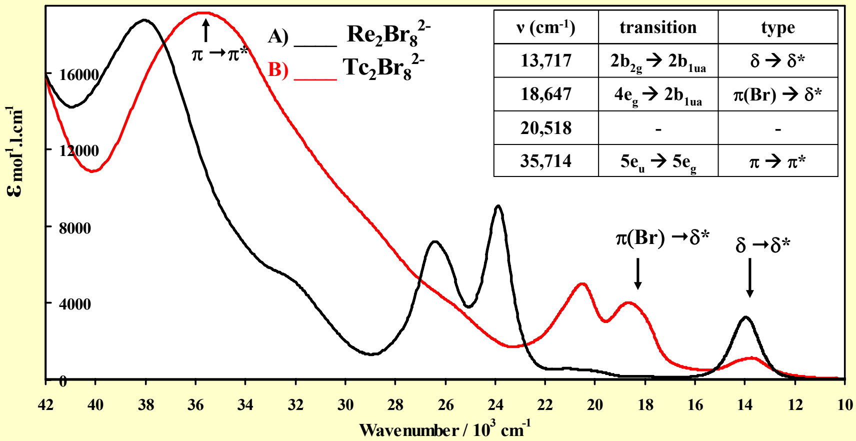
Compounds	Tc-Tc (Å)	Tc-X (Å)	<Tc-Tc-X> (°)
$(n\text{-}Bu_4N)_2Tc_2Br_8{\cdot}4[(CH_3)_2CO]$	2.1625(9)	2.4734(7)	105.01(3)
$(n\text{-}Bu_4N)_2Tc_2Cl_8$	2.147(4)	2.320(4)	103.8(4)

- Increase of Tc-Tc separation and the <Tc-Tc-Br> angle
- Steric effects induced by bromide in $[Tc_2Br_8]_{2-}$ ion

* Poineau, F. et al., *Dalton. Trans.* 2009

UV-visible spectroscopy

$(n\text{-}Bu_4N)_2M_2Br_8$ (M = Tc, Re) in CH_2Cl_2



ν (cm⁻¹)	transition	type
13,717	$2b_{2g} \rightarrow 2b_{1ua}$	$\delta \rightarrow \delta^*$
18,647	$4e_g \rightarrow 2b_{1ua}$	$\pi(Br) \rightarrow \delta^*$
20,518	-	-
35,714	$5e_u \rightarrow 5e_g$	$\pi \rightarrow \pi^*$

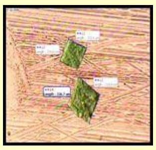
UV-visible spectrum of $Tc_2Br_8^{2-}$ similar to $Re_2Br_8^{2-}$

• Interpretation of $Tc_2Br_8^{2-}$ electronic spectra

B - $Tc_2(O_2CCH_3)_4X_2$ (X= Cl, Br)

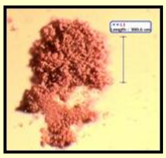
Reaction of $(n\text{-}Bu_4N)_2Tc_2X_8$ in boiling acetic acid/acetic anhydride 4:1 v/v.

Schlenk line techniques



$(n\text{-}Bu_4N)_2Tc_2Cl_8$

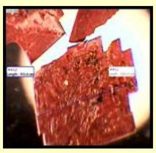
t = 20 min →



$Tc_2(O_2CCH_3)_4Cl_2$

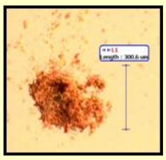
Yield = 34 %

(Air stable)



$(n\text{-}Bu_4N)_2Tc_2Br_8$

t = 3 min →



$Tc_2(O_2CCH_3)_4Br_2$

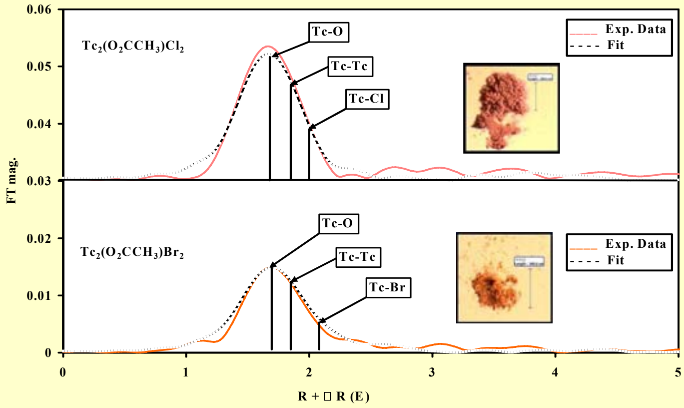
Yield = 76 %

(Air stable)

Compounds insoluble in organic solvents (CH_2Cl_2, acetonitrile, acetone, THF, …)

· No solution studies, impossible to re-crystallize

EXAFS spectroscopy

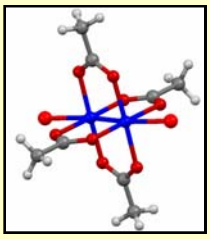


Compounds	Scattering	Structural parameter		
		C.N.	R (Å)	s2
$Tc_2(O_2CCH_3)_4Br_2$	Tc-Tc	1	2.19	0.005
	Tc-Br	0.6	2.63	0.019
$Tc_2(O_2CCH3)_4Cl_2$	Tc-Tc	1	2.18	0.0010
	Tc-Cl	0.5	2.43	0.009

Single-crystal XRD

Reaction $KTcO_4$ in HOAc/ HCl at 220 °C under H_2

(see: W. Kerlin, talk 1.12 Tuesday 14.25)



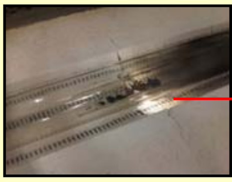
Compounds	Tc-Tc	Tc-X
$(n\text{-}Bu_4N)_2Tc_2Cl_8$	2.147(1)	2.34(2)
$(n\text{-}Bu_4N)_2Tc_2Br_8$	2.162(1)	2.4973(9)
$Tc_2(O_2CCH_3)_4Cl_2$	2.18(2)	2.43(2)
$Tc_2(O_2CCH_3)_4Br_2$	2.19(2)	2.63(2)

Elongation of ~ 0.03 Å of Tc-Tc from $(n\text{-}Bu_4N)_2Tc_2X_8$ to $Tc_2(O_2CCH_3)_4X_2$
→ Tc-Tc separation depends of the position of the X terminal ligand.

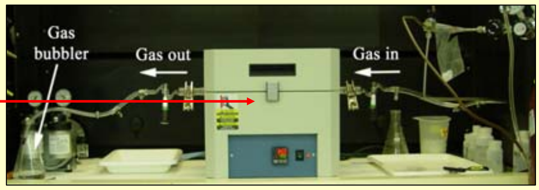
- **Axial ligand: d_{z2} orbital is shared between σ Tc-Tc and σ Tc-Cl**
- **Strong axial ligand (σ Tc-Cl) → weakening of the σ Tc-Tc bond and elongation of Tc-Tc**

C - $Tc_2(O_2CCH_3)_2Cl_4$

Reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and HCl(g) at 100°C



Tc in a quartz boat

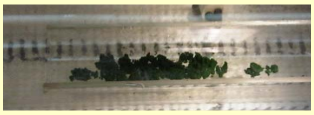


Placed in a tube furnace under flowing HCl

$Tc_2(O_2CCH_3)_4Cl_2$

~100°C

HCl(g)

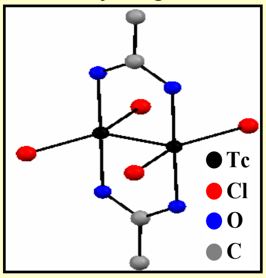


$Tc_2(O_2CCH_3)_2Cl_4$ (yield: 92%)

Highly soluble in CH_2Cl_2 and acetone

Single-crystal XRD

Crystal grown in a sealed tube under vacuum at 150°C



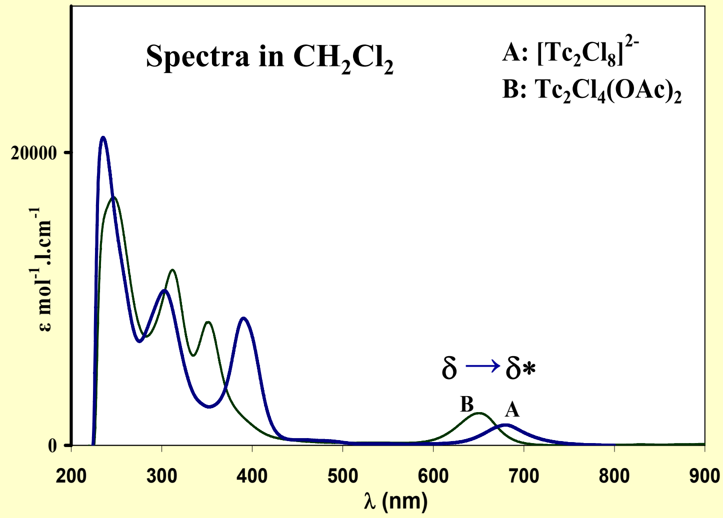
- 2 *trans*-acetate and 4 equatorial Cl
- Tc-Tc = 2.150 Å: quadruple bond
- Iso-structural to $Re_2(O_2CCH_3)_2Cl_4$
- Structural parameters similar to $Tc_2Cl_8^{2-}$

Compounds	Tc-Tc (Å)	Tc-X (Å)	<Tc-Tc-X (°)
$Tc_2(O_2CCH_3)_2Cl_4$	2.150(1)	2.312	103.0(8)
$(Bu_4N)_2Tc_2Cl_8$	2.147(4)	2.320(4)	103.8(4)

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

· Confirm influence of axial Cl ligand on Tc-Tc separation

UV-visible spectroscopy

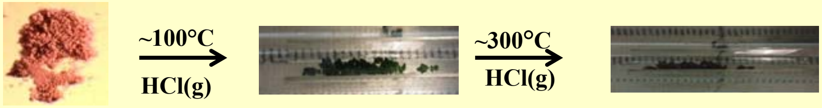


UV-visible spectra of $Tc_2(O_2CCH_3)_2Cl_4$ similar to $Tc_2Cl_8^{2-}$
· Band at 650 nm : Transition δ →δ*

II. Synthesis and characterization of Tc binary halides

A - Technetium Trichloride

Reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and HCl(g) at 350°C *

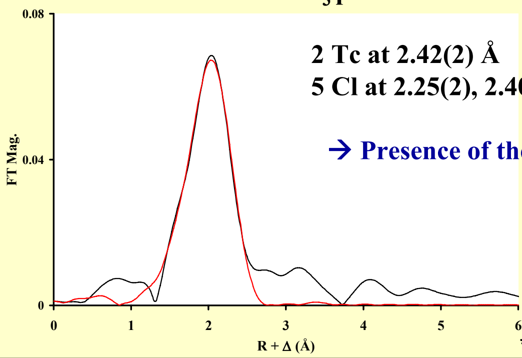


$Tc_2(O_2CCH_3)_4Cl_2$

$Tc_2(O_2CCH_3)_2Cl_4$ green crystals

$TcCl_3$: black, x-ray amorphous

EXAFS of $TcCl_3$ powder

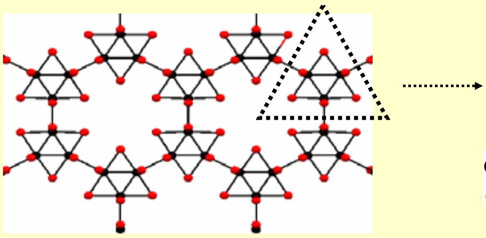


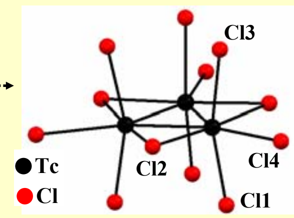
*Poineau, F., et al., *JACS*, 2010

Single-crystal XRD

Crystal grown in a sealed tube under vacuum at 450°C

Infinite layers of Tc_3Cl_9 bridged by Cl ligands (Trigonal, *R*-3m)





Tc-Tc	2.444	Tc···Tc'	3.882
$Tc-Cl_1$	2.237	$Tc-Cl_3$	2.373
$Tc-Cl_2$	2.373	$Tc-Cl_4$	2.585

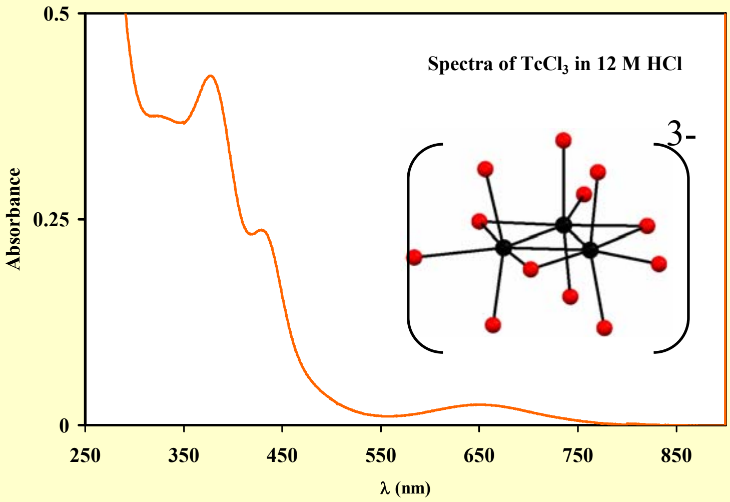
Distances (Å) in $TcCl_3$

Tc_3Cl_9 cluster in $TcCl_3$

Tc_3Cl_9 in C_{3v}
Tc in coordinance 7
Tc=Tc double bond
4 non-equivalent Cl

- $TcCl_3$ crystallize with the "$ReCl_3$" structure-type
- Calculations confirm $TcCl_3$ stability with "$ReCl_3$" structure-type
- More stable than $TcCl_3$ with the $RuCl_3$ or $MoCl_3$ structures

UV-visible Spectroscopy



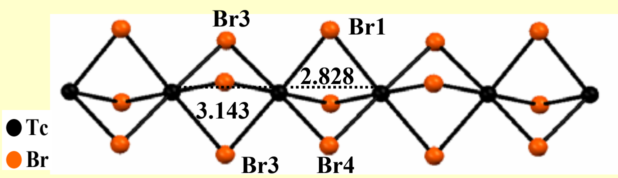
$TcCl_3$ soluble in 12 M HCl: spectra different from $[Tc_2Cl_8]^{n-}$ and $TcCl_6^{2-}$
· Analogy with Re: Formation of $[Re_3Cl_{12}]^{3-}$
· Need to perform electronic calculations

B - Technetium Tribromide

$TcBr_3$ previously synthesized from the reaction between Tc metal and Br_2 in sealed tube (Tc:Br ~ 1:3) at 350°C*

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

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



$TcBr_3$: air stable
$TcBr_6^{2-}$ in HBr(aq)

Tc-Br1	2.495	Tc-Br2	2.487
Tc-Br3	2.530	Tc-Br4	2.520

Distances (Å) in $TcBr_3$

Tc(III) d^4
O_h coordination
Alternation short/long d(Tc-Tc)
· deformation of octahedron
· Tc-Tc interaction: single bond

· Crystallizes in the "TiI_3"structure-type: iso-structural to $MoBr_3$ and $RuBr_3$
· Calculations confirm stability of $TcBr_3$ with "TiI_3" structure-type
· Predict $TcBr_3$ with $ReBr_3$ structure-type to be stable (possible dimorphism)

Reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and HBr gas at 350 °C

Room T

80 °C

- Reaction at room temperature → black powder
- Product melt/decompose at ~80 °C and converted to a black powder at 350 °C

Crystals grown in a sealed tube under vacuum at 450 °C

- Single crystal and powder XRD indicate $TcBr_3$ with the TiI_3 structure-type

- Tc_3Br_9 or/and $Tc_2(O_2CCH_3)_2Br_4$ are unstable and decompose to $TcBr_3$

C - Binary halides as precursors of low valent complexes

$MX_2(PMe_3)_4$ (X = Cl, Br) compounds are unknown in group VII

→ Metal halide reduction by Na/Hg or borohydride in presence of excess PMe_3:

$NbCl_5$	$MoCl_3(THF)_3$	Tc : ?	$RuCl_3$
$TaCl_5$	WCl_4	Re : ?	$(NH_4)_2OsCl_6$

Reaction: $TcBr_3$ and $PMe_3/NaEt_3BH$

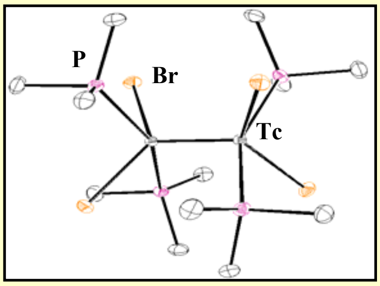
Technetium tribromide: reaction in THF with 30 mol xs PMe_3 and 1.3 eq. $NaEt_3BH$

$TcBr_3$

1. Stirring 12 hours under Ar
2. Pumping to dryness
3. Extraction and crystallization from hexane

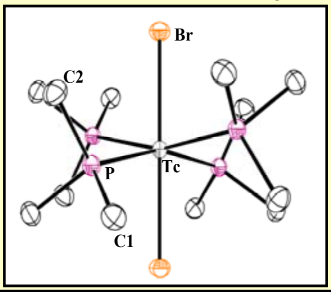
$TcBr_2(PMe_3)_4$ $Tc_2Br_4(PMe_3)_4$

A) $Tc_2Br_4(PMe_3)_4$



- First $Tc_2^{II}Br_4(PR_3)_4$ characterized*
- Triple Tc-Tc bonded dimer: $\sigma^2\pi^4\delta^2\delta^{*2}$
- Isomorphous to $M_2Br_4(PMe_3)_4$ (M = Re, Mo)

B) *trans*-$TcBr_2(PMe_3)_4$



- First $M^{II}X_2(PMe_3)_4$ for group VII
- Octahedral complex, D_{2d} symmetry
- Four equatorial PMe_3, *trans*-axial Br's
- Isomorphous to $MoBr_2(PMe_3)_4$

*Poineau, F., et al., *Dalton Trans.*, 2009

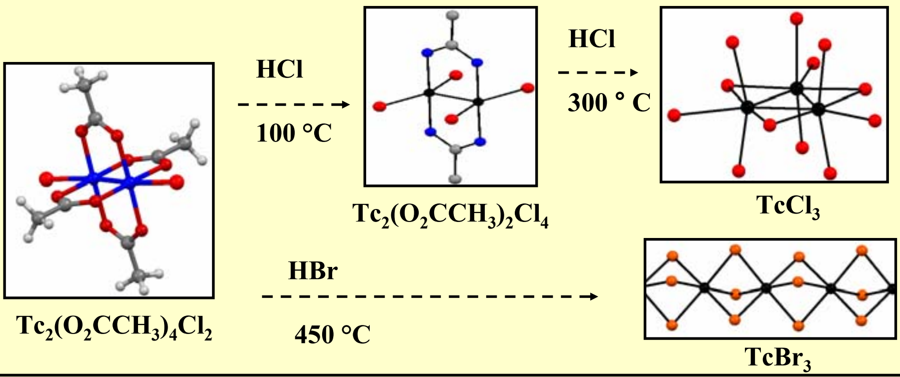
Conclusions

→ New structural data $Tc_2Br_8^{2-}$ and $Tc_2(O_2CCH_3)_4X_2$ (X = Cl, Br)

· Influence of X (Cl, Br) nature and position on Tc-Tc separation
· Axial X ligand in $Tc_2(O_2CCH_3)_2Cl_4$ → larger Tc-Tc separation
· Br induces more steric congestion in $Tc_2X_8^{2-}$ than Cl ligand → Tc-Tc elongation

→ Reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and HX(g) (X= Cl, Br)

· One novel quadruple Tc-Tc bonded dimer: $Tc_2(O_2CCH_3)_2Cl_4$
· Two new binary halides: $TcCl_3$ and $TcBr_3$
· For X = Cl, mechanism similar to Re, $Tc_2(O_2CCH_3)_2Cl_4$ intermediate
· For X = Br, Tc_3Br_9 or/and$Tc_2(O_2CCH_3)_2Br_4$ unstable and decompose



→ Comparison with neighboring elements

· Polymorphism of Tc trihalides

$TcBr_3$ similar to $RuBr_3$ and $MoBr_3$, while $TcCl_3$ is similar to $ReCl_3$

→ Structure and bonding in TcX_3

· For X = Cl, Tc-Tc = 2.444 Å → double bond
UV-visible in HCl(aq): Possible formation of $[Tc_3Cl_{12}]^{3-}$
· For X = Br, Tc-Tc = 2.828 Å → single bond
UV-visible in HBr(aq): Oxidation to $TcBr_6^{2-}$

→ Use of binary halide as precursors

Reaction of $TcBr_3$ with PMe_3/$NaEt_3BH$: 2 new complexes
· *trans*-$TcBr_2(PMe_3)_4$ and $Tc_2Br_4(PMe_3)_4$

Future Work

Continue to investigate molecular complexes for binary halides

Tc-iodide: TcI_3 by reaction between $Tc_2(OCCH_3)_4Cl_2$ under HI gas
Tc-bromide: Reaction between $TcCl_3$ with HBr gas
Tc-chloride: Investigation of Tc dichloride → **E. Johnstone, talk 1.13 Tuesday 14.50.**

New reactions using Tc binary halides as precursors

Conversion of $TcCl_3$ to molecular $Tc_3Cl_9L_3$ (e.g., L = PR_3) complexes

Acknowledgments

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Radiation protection and Health Physics

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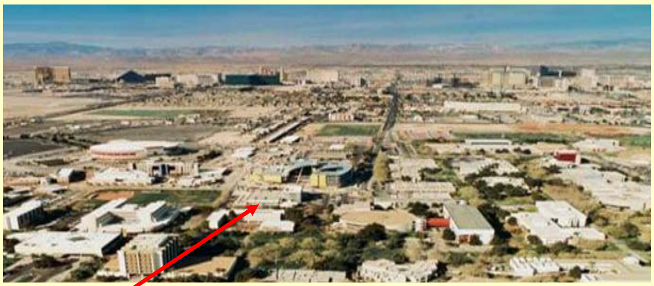
Questions



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