Technetium Binary Halides: from Molecular to Extended Structures

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Fundamental and Applied Research on Technetium

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

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

Chemistry relevant to radiopharmaceuticals
- ⁹⁹Tc nitrosyl and phosphine complexes

Better understand fundamental chemistry
⇒ New applications (waste form, separations…)
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-Bu₄N)₂Tc₂Br₈
   B - Tc₂(O₂CCH₃)₂X₂ (X = Cl, Br)
   C - Tc₂(O₂CCH₃)₂Cl₂

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
- Known for group VI and VII; ~ 300 for Mo and ~100 for Re
- Five Tc quadruple bonded dimers structurally characterized:
  \((n-\text{Bu}_4\text{N})_2\text{Tc}_2\text{Cl}_8\), \(\text{Tc}_2(\text{O}_2\text{CCMe}_3)_4\text{Cl}_2\), \(\text{Tc}_2(\text{O}_2\text{CMc})_4(\text{TeO}_4)_2\), \(\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4\cdot2\text{dma}\) and \(\text{K}_2\text{Tc}_2(\text{SO}_4)_4\cdot2\text{H}_2\text{O}\)
- No bromides or iodides have been structurally characterized
  \((n-\text{Bu}_4\text{N})_2\text{Tc}_2\text{Br}_8\) and \(\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{X}_2\) (X = Cl, Br) previously reported, but not well characterized

Transition metal binary halides

- \(\text{MX}_n\) (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 \(\text{H}X\) (X = Cl, Br, I) gas
- Only three technetium binary halides: \(\text{TcCl}_4\), \(\text{TcF}_6\) and \(\text{TcF}_5\)

- No binary iodides and bromides known
- No trivalent or divalent Tc binary halides reported
- No reaction involving molecular complexes and \(\text{H}X\) gas reported
GOAL

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

- Structure and bonding of Tc₂Br₈²⁻ and Tc₂(Ο₂CCH₃)₄X₂ (X = Cl, Br)
- Synthesis of binary halide from reaction Tc₂(Ο₂CCH₃)₄Cl₂ 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 - \((n{-}\text{Bu}_4\text{N})_2\text{Tc}_2\text{Br}_8\)

**Preparation**

\[
\begin{align*}
\text{TcO}_2/\text{NH}_4\text{TcO}_4 & \quad (n{-}\text{Bu}_4\text{N})\text{TcO}_4 & \quad (n{-}\text{Bu}_4\text{N})\text{TcOCl}_4 \\
\rightarrow & \quad 12 \text{ M HCl} & \quad 12 \text{ M HCl} \\
\rightarrow & \quad T = 0 ^\circ \text{C} & \quad \text{H}_2\text{O}_2,
\end{align*}
\]

\[
\begin{align*}
(n{-}\text{Bu}_4\text{N})\text{Tc}_2\text{Br}_8 & \quad (n{-}\text{Bu}_4\text{N})\text{Tc}_2\text{Cl}_8 & \quad (n{-}\text{Bu}_4\text{N})\text{BH}_4 \\
\rightarrow & \quad \text{HBr gas} & \quad \text{HCl, acetone} \\
\rightarrow & \quad T = 30 ^\circ \text{C} & \quad \text{THF} \\
\end{align*}
\]

**Single-crystal XRD**

Recrystallization from acetone/ether provides single crystals → Formation of an acetone solvate: \((n{-}\text{Bu}_4\text{N})_2\text{Tc}_2\text{Br}_8\cdot 4[(\text{CH}_3)_2\text{CO}]^*

View of the solvate from the a direction

\[
\begin{align*}
\text{Tc}_2\text{Br}_8^{2-} & \text{ ion} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Tc-Tc (Å)</th>
<th>Tc-X (Å)</th>
<th>(&lt;\text{Tc-Tc-X}&gt; (^\circ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((n{-}\text{Bu}_4\text{N})_2\text{Tc}_2\text{Br}_8\cdot 4[(\text{CH}_3)_2\text{CO}])</td>
<td>2.1625(9)</td>
<td>2.4734(7)</td>
<td>105.01(3)</td>
</tr>
<tr>
<td>((n{-}\text{Bu}_4\text{N})_2\text{Tc}_2\text{Cl}_8)</td>
<td>2.147(4)</td>
<td>2.320(4)</td>
<td>103.8(4)</td>
</tr>
</tbody>
</table>

- Increase of Tc-Tc separation and the \(<\text{Tc-Tc-Br}> angle
- Steric effects induced by bromide in \([\text{Tc}_2\text{Br}_8])_2\ ion

\* Poineau, F. et al., *Dalton. Trans.*, 2009
UV-visible spectroscopy

\[(\text{n-Bu}_4\text{N})_2\text{M}_2\text{Br}_8 (\text{M} = \text{Tc}, \text{Re}) \text{ in CH}_2\text{Cl}_2\]

<table>
<thead>
<tr>
<th>v (cm(^{-1}))</th>
<th>transition</th>
<th>type</th>
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<tbody>
<tr>
<td>13,717</td>
<td>2b(<em>{2g}) → 2b(</em>{1u})</td>
<td>δ → δ*</td>
</tr>
<tr>
<td>18,647</td>
<td>4e(<em>g) → 2b(</em>{1u})</td>
<td>π(Br) → δ*</td>
</tr>
<tr>
<td>20,518</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35,714</td>
<td>5e(_g) → 5e(_g)</td>
<td>π → π*</td>
</tr>
</tbody>
</table>

UV-visible spectrum of Tc\(_2\)Br\(_8\)^{2-} similar to Re\(_2\)Br\(_8\)^{2-}:
- Interpretation of Tc\(_2\)Br\(_8\)^{2-} electronic spectra

**B - Tc\(_2\)(O\(_2\)CCH\(_3\))\(_4\)X\(_2\) (X= Cl, Br)**

Reaction of (n-Bu\(_4\)N)\(_2\)Tc\(_2\)X\(_8\) in boiling acetic acid/acetic anhydride 4:1 v/v.

\((\text{n-Bu}_4\text{N})_2\text{Tc}_2\text{Cl}_8\)

Yield = 34 %
(Air stable)

\((\text{n-Bu}_4\text{N})_2\text{Tc}_2\text{Br}_8\)

Yield = 76 %
(Air stable)

Compounds insoluble in organic solvents (CH\(_2\)Cl\(_2\), acetonitrile, acetone, THF, …)
- No solution studies, impossible to re-crystallize
EXAFS spectroscopy

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Scattering</th>
<th>Structural parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C.N.</td>
<td>R (Å)</td>
</tr>
<tr>
<td>Tc₂(O₂CCH₃)₄Br₂</td>
<td>Te-Te</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Te-Br</td>
<td>0.6</td>
</tr>
<tr>
<td>Tc₂(O₂CCH₃)₄Cl₂</td>
<td>Te-Te</td>
<td>1</td>
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<tr>
<td></td>
<td>Te-Cl</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Elongation of ~ 0.03 Å of Tc-Tc from (n-Bu₄N)₂Tc₂X₈ to Tc₂(O₂CCH₃)₄X₂

Tc-Tc separation depends on the position of the X terminal ligand.

• Axial ligand: $d_{dz^2}$ orbital is shared between $\sigma$ Tc-Tc and $\sigma$ Tc-Cl
• Strong axial ligand (σ Tc-Cl) $\Rightarrow$ weakening of the σ Tc-Tc bond and elongation of Tc-Tc

Single-crystal XRD

Reaction KTCO₄ in HOAc/ HCl at 220 °C under H₂

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

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Te-Tc</th>
<th>Te-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n-Bu₄N)₂Tc₂Cl₈</td>
<td>2.147(1)</td>
<td>2.34(2)</td>
</tr>
<tr>
<td>(n-Bu₄N)₂Tc₂Br₈</td>
<td>2.162(1)</td>
<td>2.4973(9)</td>
</tr>
<tr>
<td>Tc₂(O₂CCH₃)₄Cl₂</td>
<td>2.18(2)</td>
<td>2.43(2)</td>
</tr>
<tr>
<td>Tc₂(O₂CCH₃)₄Br₂</td>
<td>2.19(2)</td>
<td>2.63(2)</td>
</tr>
</tbody>
</table>

Elongation of ~ 0.03 Å of Tc-Tc from (n-Bu₄N)₂Tc₂X₈ to Tc₂(O₂CCH₃)₄X₂

$\Rightarrow$ Tc-Tc separation depends on the position of the X terminal ligand.
C - Tc$_2$(O$_2$CCH$_3$)$_2$Cl$_4$

Reaction between Tc$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ and HCl(g) at 100°C

Tc in a quartz boat

Placed in a tube furnace under flowing HCl

~100°C

HCl(g)

Tc$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ → Tc$_2$(O$_2$CCH$_3$)$_2$Cl$_4$ (yield: 92%)

Highly soluble in CH$_2$Cl$_2$ 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$_2$CCH$_3$)$_4$Cl$_4$
- Structural parameters similar to Tc$_2$Cl$_8$²⁻

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Tc-Tc (Å)</th>
<th>Tc-X (Å)</th>
<th>&lt;Tc-Tc-X (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc$_2$(O$_2$CCH$_3$)$_4$Cl$_2$</td>
<td>2.150(1)</td>
<td>2.312</td>
<td>103.0(8)</td>
</tr>
<tr>
<td>(Bu$_4$N)$_2$Tc$_2$Cl$_8$</td>
<td>2.147(4)</td>
<td>2.320(4)</td>
<td>103.8(4)</td>
</tr>
</tbody>
</table>

Decrease of Tc-Tc from Tc$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ to Tc$_2$(O$_2$CCH$_3$)$_2$Cl$_4$

- Confirm influence of axial Cl ligand on Tc-Tc separation
II. Synthesis and characterization of Tc binary halides
A - Technetium Trichloride

Reaction between Tc₂(O₂CCH₃)₄Cl₂ and HCl(g) at 350°C *

- Tc₂(O₂CCH₃)₄Cl₂: green crystals
- TcCl₃: black, x-ray amorphous

EXAFS of TcCl₃ powder

2 Tc at 2.42(2) Å
5 Cl at 2.25(2), 2.40(2), 2.50(3) Å

→ Presence of the Tc₃Cl₉ unit

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

Single-crystal XRD

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

Infinite layers of Tc₃Cl₉ bridged by Cl ligands (Trigonal, R-3m)

- Tc-Tc 2.444 Å
- Te-Te 3.882 Å
- Te-Cl₁ 2.237 Å
- Te-Cl₂ 2.373 Å
- Te-Cl₃ 2.373 Å
- Te-Cl₄ 2.585 Å

Tc₃Cl₉ cluster in TeCl₃

Tc₃Cl₉ in C₃v
Tc in coordination 7
Tc-Tc double bond
4 non-equivalent Cl

TcCl₃ crystallize with the “ReCl₃” structure-type
Calculations confirm TcCl₃ stability with “ReCl₃” structure-type
More stable than TcCl₃ with the RuCl₃ or MoCl₃ structures
UV-visible Spectroscopy

Spectra of TcCl₃ in 12 M HCl

TcCl₃ soluble in 12 M HCl: spectra different from [Tc₂Cl₈]³⁻ and TcCl₆²⁻
- Analogy with Re: Formation of [Re₂Cl₈]³⁻
- Need to perform electronic calculations

B - Technetium Tribromide

TcBr₃ previously synthesized from the reaction between Tc metal and Br₂ in sealed tube (Tc:Br ~ 1:3) at 350°C
- Poineau, F et al., JACS, 2009

TcBr₃: Infinite chains of face-sharing TcBr₆ octahedra

Tc(III) d⁵
O₆ coordination
- Alternation short/long d(Tc-Tc)
- deformation of octahedron
- Tc-Tc interaction: single bond

Distances (Å) in TcBr₃

<table>
<thead>
<tr>
<th></th>
<th>Tc-Br1</th>
<th>Tc-Br2</th>
<th>Tc-Br3</th>
<th>Tc-Br4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc-Br1</td>
<td>2.495</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc-Br3</td>
<td>2.530</td>
<td>2.520</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Crystallizes in the “TiI₃” structure-type: iso-structural to MoBr₃ and RuBr₃
- Calculations confirm stability of TcBr₃ with “TiI₃” structure-type
- Predict TcBr₃ with ReBr₃ structure-type to be stable (possible dimorphism)
Reaction between $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and HBr gas at 350 °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 $\text{TcBr}_3$ with the TiI$_3$ structure-type

- $\text{Tc}_3\text{Br}_9$ or/and $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Br}_4$ are unstable and decompose to $\text{TcBr}_3$

C - Binary halides as precursors of low valent complexes
$\text{MX}_2(\text{PMe}_3)_4$ ($\text{X} = \text{Cl, Br}$) compounds are unknown in group VII

→ Metal halide reduction by Na/Hg or borohydride in presence of excess PMe$_3$:

| $\text{NbCl}_5$ | $\text{MoCl}_5(\text{THF})_3$ | Tc : ? | $\text{RuCl}_3$ |
| $\text{TaCl}_5$ | $\text{WCl}_4$ | Re : ? | ($\text{NH}_4$)$_2\text{OsCl}_6$ |

Reaction: $\text{TcBr}_3$ and PMe$_3$/NaEt$_3$BH

Technetium tribromide: reaction in THF with 30 mol xs PMe$_3$ and 1.3 eq. NaEt$_3$BH

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

$\text{TcBr}_3$ $\text{PMe}_3$ $\text{NaEt}_3$ $\text{BH}$
A) $\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4$

- First $\text{Tc}^{II}\text{Br}_4(\text{PR}_3)_4$ characterized
- Triple Tc-Tc bonded dimer: $\sigma^2\pi^4\delta^6\delta^2$
- Isomorphous to $\text{M}_2\text{Br}_4(\text{PMe}_3)_4$ ($\text{M} = \text{Re}, \text{Mo}$)

B) $\text{trans-TeBr}_2(\text{PMe}_3)_4$

- First $\text{M}^{II}\text{X}_2(\text{PMe}_3)_4$ for group VII
- Octahedral complex, $D_{2d}$ symmetry
- Four equatorial PMe$_3$, $\text{trans}$-axial Br’s
- Isomorphous to $\text{MoBr}_2(\text{PMe}_3)_4$

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

Conclusions
New structural data $\text{Tc}_2\text{Br}_8^{2-}$ and $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$)
- Influence of $\text{X}$ (Cl, Br) nature and position on Te-Tc separation
- Axial X ligand in $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_4$ → larger Te-Tc separation
- Br induces more steric congestion in $\text{Tc}_2\text{X}_8^{2-}$ than Cl ligand → Te-Tc elongation

Reaction between $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and HX(g) ($\text{X} = \text{Cl}, \text{Br}$)
- One novel quadruple Te-Tc bonded dimer: $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_4$
- Two new binary halides: $\text{TcCl}_3$ and $\text{TcBr}_3$
- For $\text{X} = \text{Cl}$, mechanism similar to Re, $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_4$ intermediate
- For $\text{X} = \text{Br}$, $\text{Tc}_3\text{Br}_9$ or $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Br}_4$ 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 $\text{X} = \text{Cl}$, Te-Tc = 2.444 Å → double bond
  - UV-visible in HCl(aq): Possible formation of $[\text{Tc}_3\text{Cl}_{12}]^{3-}$
- For $\text{X} = \text{Br}$, Te-Tc = 2.828 Å → single bond
  - UV-visible in HBr(aq): Oxidation to $\text{TcBr}_6^{2-}$

Use of binary halide as precursors
- Reaction of TcBr$_3$ with PMe$_3$/NaEt$_3$BH: 2 new complexes
  - $\text{trans}$-TcBr$_2$(PMe$_3$)$_4$ and Tc$_2$Br$_4$(PMe$_3$)$_4$
Future Work

**Continue to investigate molecular complexes for binary halides**

- Tc-iodide: TcI₃ by reaction between Tc₂(OCCH₃)₄Cl₂ under HI gas
- Tc-bromide: Reaction between TcCl₃ with HBr gas
- Tc-chloride: Investigation of Tc dichloride

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E. Johnstone, talk 1.13
Tuesday 14.50.

**New reactions using Tc binary halides as precursors**

Conversion of TcCl₃ to molecular Tc₃Cl₉L₃ (e.g., L = PR₃) complexes

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Acknowledgments

Mr. Tom O’Dou

Radiation protection and Health Physics

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Questions

Radiochemistry Program at the University of Nevada Las Vegas

For more information, please visit http://Radchem.nevada.edu