Preparation of Technetium Metal-Metal Bonded Acetate Dimers via Autoclave Route

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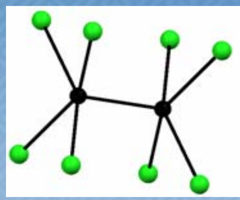
Overview

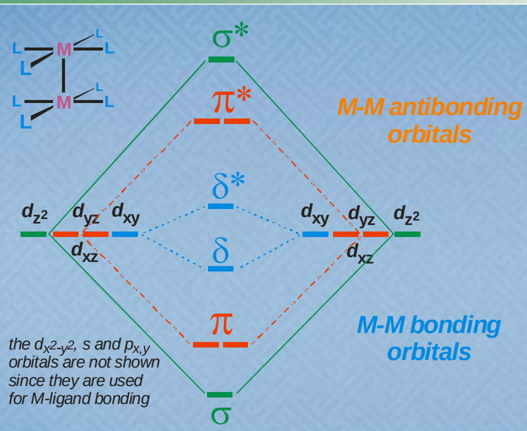
- Introduction
- Our Tools and Methods
- Results
- Conclusions

Introduction



- Quadruple Metal-Metal dimers
  - Cotton, A. 1964, $Re_2Cl_8^{-2}$
- Known compounds of Acetate Dimers
  - Tc_2^{+6} core
    - $Tc_2(\mu\text{-}O_2CCH_3)_4X_2$ (X= Cl, Br)
    - $Tc_2(\mu\text{-}O_2CCH_3)_2Cl_2 \cdot (dma)_2$
    - $Tc_2(\mu\text{-}O_2CCH_3)_2Cl_2 \cdot (H_2O)_2$
    - $Tc_2(\mu\text{-}O_2CCH_3)_4(TcO4)_2$
  - Tc_2^{+5} core
    - $Tc_2(\mu\text{-}O_2CCH_3)_4X$ (X= Cl, Br)
    - $K[Tc_2(\mu\text{-}O_2CCH_3)_4X_2]$ (X= Cl, Br)

Metal – Metal Multiple Bonds



Electron Count	Resulting M-M Bond
d1 - d1	Single bond
d2 - d2	Double bond
d3 - d3	Triple bond
d4 - d4	Quadruple bond *optimum*
d5 - d5	Triple bond
d6 - d6	Double bond *(M-L bonding usually dominates)*
d7 - d7	Single bond
d8 - d8	No bond *(symmetry interaction)*

$$\text{Bond Order} = \frac{\text{Bonding Orbital } e^- - \text{Antibonding Orbital } e^-}{2} = \frac{8-0}{2} = 1$$

Approximate MO diagram for M-M bond (square planar ligands) From chemistry.lus.edu/stanley/web4571-notes/chap10-mm-bonding.doc

Three Autoclave Systems: Our Tools

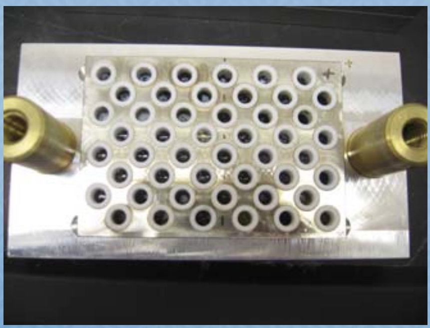
1. Parr 4749 General Purpose Bomb, Autoclave

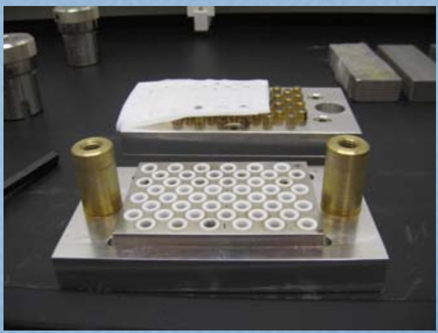
Max. Temp.
~ 250°C
Max. Pressure
120 atm
Volume
23 mL

http://www.parrinst.com

2. Multi-well Autoclave

Exploratory reactions over a large range of conditions
Max. Temp. 250°C, Pressure 25 atm, Volume 350 μL





Parr 5500 Series High Pressure Controlled Atmosphere Autoclave

- Max. Temp. 350 °C
- Max. Pressure
  - 200 atm
- Volume
  - 300 mL
- Atmosphere
  - Inert
  - Reducing

Conventional Preparation: $Tc_2(O_2CCH_3)_4Cl_2$

TcO_2/NH_4TcO_4

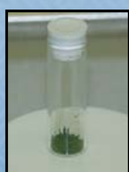
$T = 100\ °C,\ H_2O_2$ → $(n\text{-}Bu_4N)OH$

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

12 M HCl → T = 0 °C

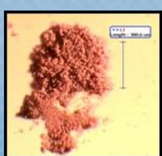
$(n\text{-}Bu_4N)TcOCl_4$

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



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

← Acetic Acid/ Acetic Anhydride 4:1 v/v, t = 20 min

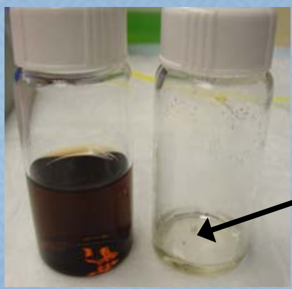


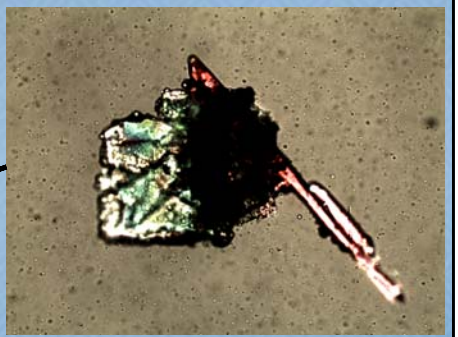
$Tc_2(O_2CCH_3)_4Cl_2$

Yield = 10 %
(Air stable)

Experimental Method

*$KTcO_4$ + 2:1 $HC_2H_3O_2$:HCl $\xrightarrow[\text{210 °C, 12 hr}]{\text{36 atm } H_2}$





- Red/Pink Crystals: $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$
- Turquoise Blue Crystals: $Tc_2(\mu\text{-}O_2CCH_3)_3Cl_2(H_2O)_2 \cdot H_20$

* L. I. Zaitseva, A.S. Kotel'nikova and A.A. Reszvov, *Russ. J. Inorg. Chem.* 1980, **25**, 1449

Single Crystal XRD
$Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$

- Quadruple bond
- Tc_2^{+6} core, Tc(III)

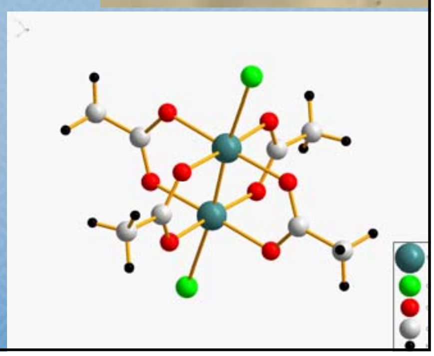
Space Group: Monoclinic, $P2_1/n$

Unit Cell

a=6.4258(8) Å
b=8.8474(11) Å
c=12.5285(16) Å
β=90.778(2)°
V=712.20(15) Å^3

Key Bond Distances:

- Tc-Tc 2.1758(3) Å
- Tc-Cl 2.5078(4) Å
- Tc-O 2.021 Å(average)



Single Crystal XRD
$Tc_2(\mu\text{-}O_2CCH_3)_3Cl_2(H_2O)_2 \cdot H_20$

- 3.5 bond order
- Tc_2^{+5} core

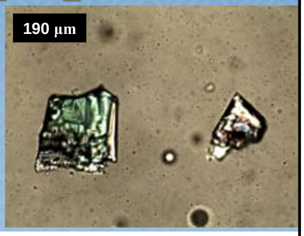
Space Group: Monoclinic, $P2_1$

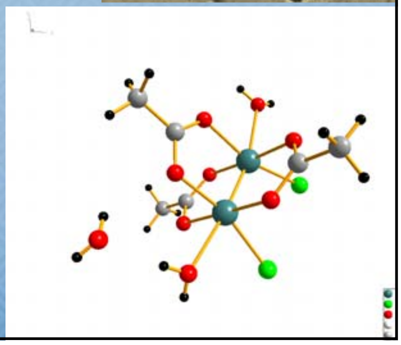
Unit Cell

a=7.7102(7) Å
b=11.4786(11) Å
c=8.3468(8) Å
β=94.843(1)°
V=736.07(12) $Å^3$

Key Bond Distances:

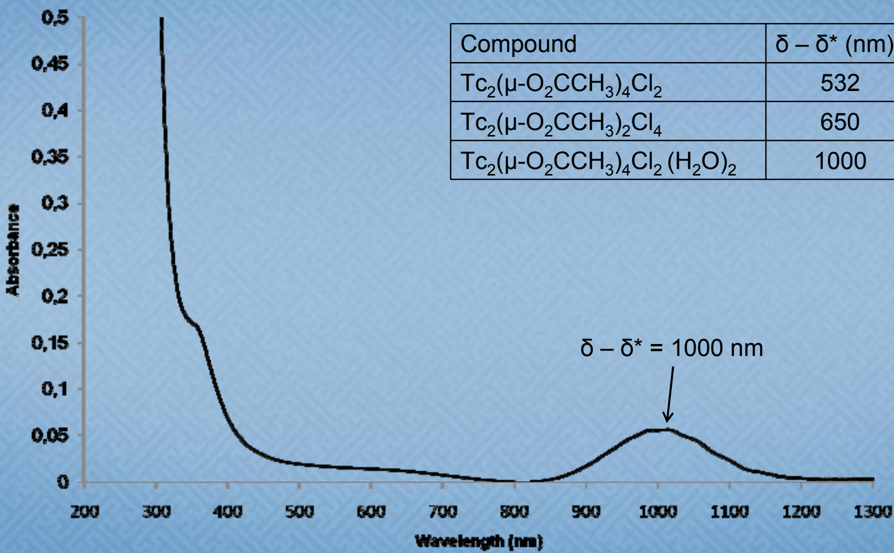
- Tc-Tc 2.1152(1) Å
- Tc-Cl 2.3566(4) Å (average)





Absorbance Spectrum
$Tc_2(\mu\text{-}O_2CCH_3)_3Cl_2(H_2O)_2 \cdot H_2O$

Compound	δ – δ* (nm)
$Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$	532
$Tc_2(\mu\text{-}O_2CCH_3)_2Cl_4$	650
$Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2\,(H_2O)_2$	1000



Skowronek, J.; Preetz, W. Zeitschrift fuer Naturforschung, B. (1992), 47(4), 482-90.

Proposed Mechanism?

- Reduction Step
  - $TcO_4^- \rightarrow TcCl_6^{2-} \rightarrow Tc_2Cl_8^{3-} \rightarrow Tc_2Cl_2(OAc)_3(H_2O)_2$
- Oxidation in Air
  - $Tc_2Cl_2(OAc)_3(H_2O)_2 \rightarrow Tc_2Cl_2(OAc)_4$

- Use Uv-vis absorbance optical Dip-probe to monitor reaction over time.
  - Observe delta-delta* transition of Metal-Metal Bond

*Kryuchkov, S.V.; Kuzina, A. F.; Spitsyn, V. I. New technetium halide clusters. Akademii Nauk SSSR (1982), 266(1), 127-30

Conclusion

- Single Crystal Structures
  - $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$
  - New Compound Produced
    - $Tc_2(\mu\text{-}O_2CCH_3)_3Cl_2(H_2O)_2{\cdot}H_20$
- One Step Process
  - 70 % yield, $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$
- Future Work
  - Hydrobromic acid and Hydroiodic acid reactions
  - Continue work on production of intermediates for Tc halide synthesis

Acknowledgements

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  - Tom O'Dou, Trevor Low, Julie Bertoia

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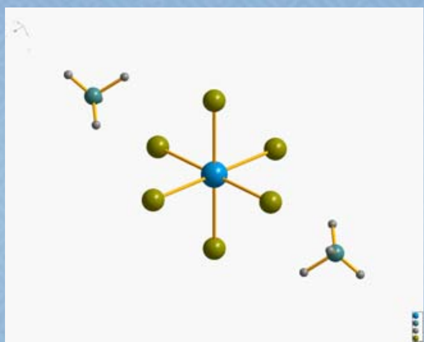
Questions?

HBr Reaction: $(NH_4)_2TcBr_6$

- Tc oxidation state +4
- Single Crystal Structure Unknown
- Elongated N-H bond
  - 1.0334 Å N-H
  - 1.1622 Å N-H
    - Hydrogen Bonding???



Space Group: Trigonal, R 3m

Unit Cell

a=7.3121(6) Å b=7.3121(6) Å
c=17.9078(27) Å
V=892.20(18) $Å^3$

Key Bond Distances:

- Tc-Br 2.5049(2) Å (average)