



STRUCTURAL CHEMISTRY OF TECHNETIUM CARBONYL COMPOUNDS

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Structurally characterized technetium carbonyl complexes

- Tc(III) compounds: 7-coordinate:

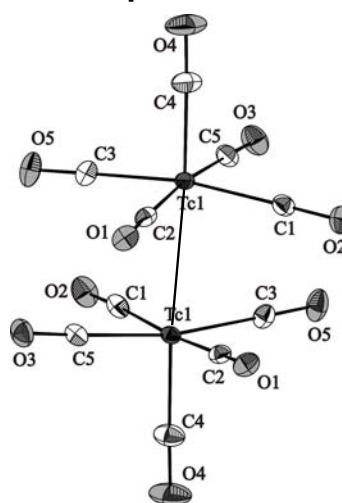
$\text{Tc}(\text{Et}_2\text{NCS}_2)_3(\text{CO})$,
 $\text{TcCl}_3(\text{PR}_3)_3(\text{CO})$,
 $\text{Tc}(\text{C}_5\text{Me}_5)\text{Br}(\text{CO})_3^+$,
 $\text{Tc}(\text{C}_5\text{Me}_5)\text{Br}_2(\text{CO})_2$;

5-coordinate:

$\text{Tc}(\text{durenethiolate})_3(\text{CO})\text{L}$

- Tc(I) compounds: the most numerous group, discussed in detail below

- Tc(0) compounds: $\text{Tc}_2(\text{CO})_{10}$,
 $\text{Tc}_2(\text{CO})_8(\text{diene})$,
 $\text{Tc}_2(\text{CO})_8(\text{pyridine})_2$



Technetium decacarbonyl

Chemical forms of mononuclear Tc(I) carbonyls $Tc(CO)_nL_m$

- $n = 6$: $Tc(CO)_6^+$
- $n = 5$: $Tc(CO)_5M$
- $n = 4$: $Tc(CO)_4B$ [no data for $Tc(CO)_4M_2$]
- $n = 3$: $Tc(CO)_3M_3$, $Tc(CO)_3BM$, $Tc(CO)_3T$
(the most numerous group)
- $n = 2$: $Tc(CO)_2M_4$, $Tc(CO)_2BM_2$, $Tc(CO)_2TM$
- $n = 1$: $Tc(CO)TM_2$

Ligands: M, monodentate; B, bidentate; T, tridentate; charge omitted.
 $n = 1$ and 2 : only with π -acceptor ligands like phosphines

trans-Effect in technetium carbonyls

σ, π -donor–Tc– π -acceptor: **favorable**;

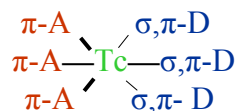
π -acceptor–Tc– π -acceptor: **unfavorable**;

CO group: typical π -acceptor (π -A); other π -acceptors: NO^+ , RNC , PR_3

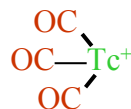
O-, N-donor ligands: typical σ -donors (σ -D);

Cp: typical π -donor

The most stable structure
(*fac*-configuration):

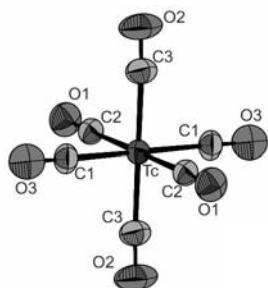


Stable structural fragment:

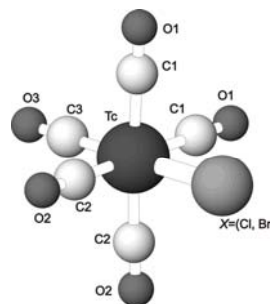


Examples of higher technetium carbonyls

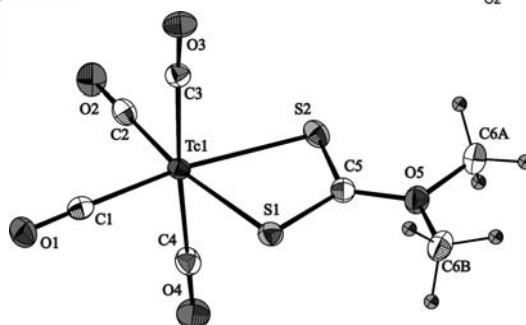
$\text{Tc}(\text{CO})_6^+$ (perchlorate)



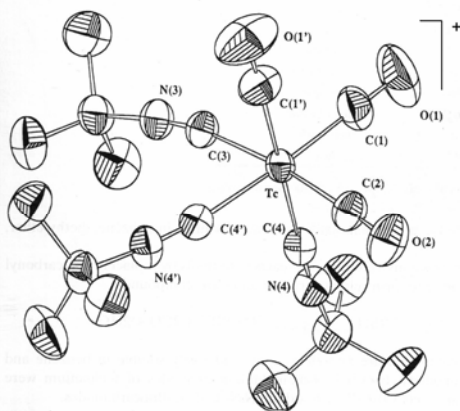
$\text{Tc}(\text{CO})_5\text{M}$ (M = Cl, Br)



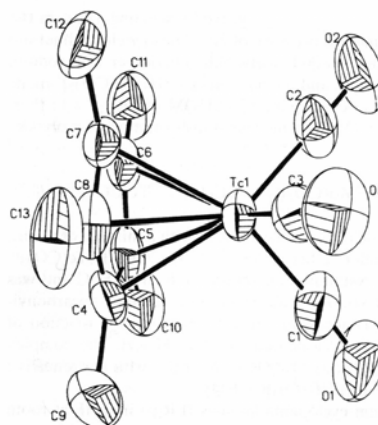
$\text{Tc}(\text{CO})_4\text{B}$ (B = xanthate, OMe disordered)



Examples of technetium tricarbonyl complexes: $\text{Tc}(\text{CO})_3\text{M}_3$ and $\text{Tc}(\text{CO})_3\text{T}$

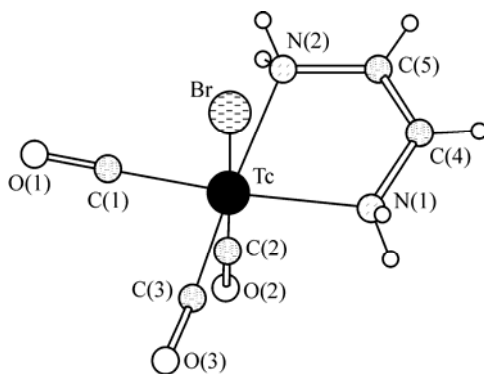


$[\text{Tc}(\text{CO})_3(\text{Bu}^4\text{NC})_3]^+$ (nitrate)
[Alberto et al., 1996]

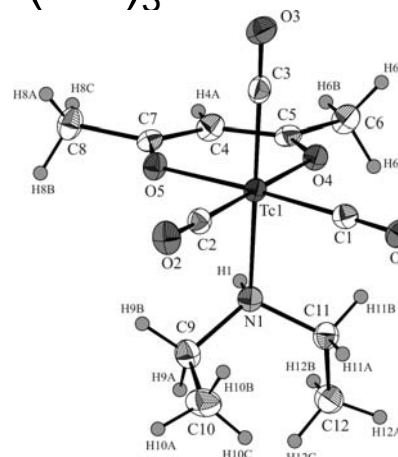


$\text{Tc}(\text{C}_5\text{Me}_5)(\text{CO})_3$
[Raptis et al., 1991]

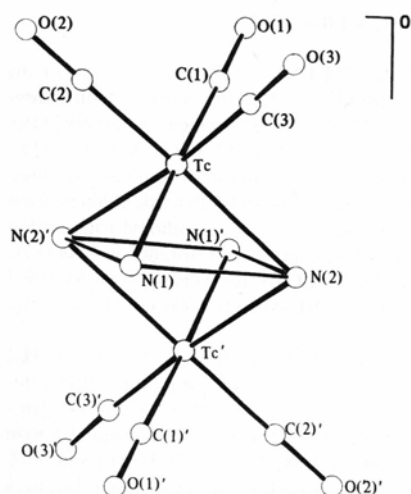
Examples of technetium tricarbonyl complexes: $\text{Tc}(\text{CO})_3\text{BM}$



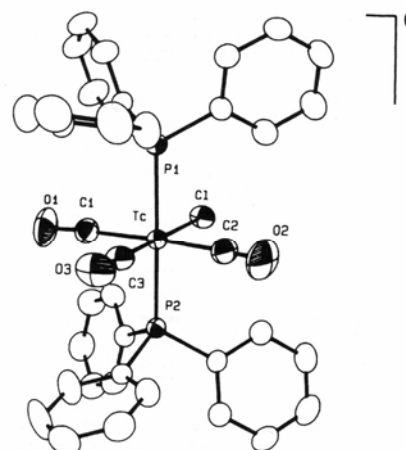
M anionic, B neutral:
 $[\text{TcBr}(\text{CO})_3(\text{en})]$
 (en = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)



B anionic, M neutral:
 $[\text{Tc}(\text{acac})(\text{CO})_3(\text{Et}_2\text{NH})]$
 (acac = $\text{CH}_3\text{COCHCOCH}_3$)

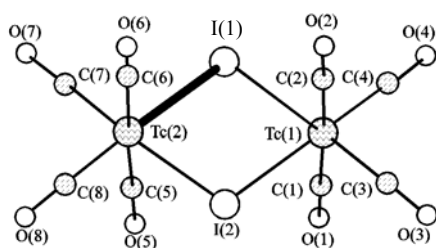


$[\text{Tc}(\text{CO})_3]_2(\text{meso-tetraphenylporphine})$:
fac- $\text{Tc}(\text{CO})_3$ core dictates unusual
 coordination of porphine
 [Tsutsui et al., 1975]

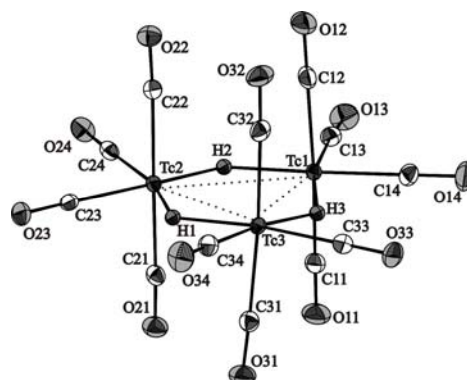


mer Structure with a bulky
 π -acceptor: $\text{TcCl}(\text{CO})_3(\text{PPh}_3)_2$
 [Alberto et al., 1992]

Polynuclear complexes $[\text{TcX}(\text{CO})_4]_n$

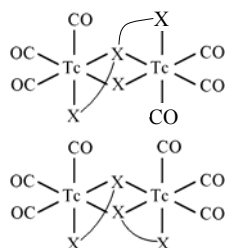


X = I: binuclear complex



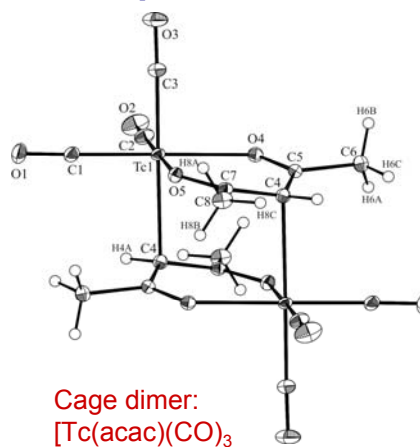
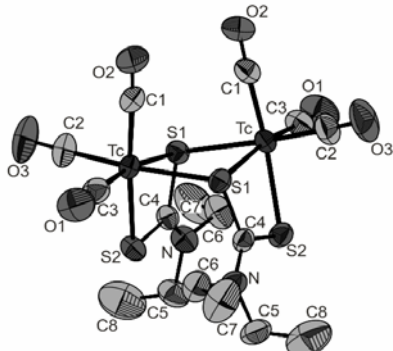
X = H: trinuclear triangular complex
with weak $\text{Tc}\cdots\text{Tc}$ bonding
[Alberto et al., 1996; our data, 2011]

Dimers $[\text{Tc}(\text{CO})_3\text{B}]_2$



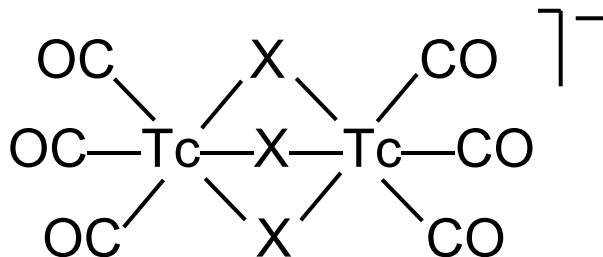
Trans (centrosymmetric), $[\text{Tc}(\text{salbut})(\text{CO})_3]_2$,
salbut = $o\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_4\text{H}_9$
[Takayama et al., 2005]

Cis (noncentrosymmetric):
 $[\text{Tc}(\text{Et}_2\text{NCS}_2)(\text{CO})_3]_2$



Cage dimer:
 $[\text{Tc}(\text{acac})(\text{CO})_3]_2$
(acac = $\text{CH}_3\text{COCHCOCH}_3$)

Binuclear anions $[\text{Tc}_2\text{X}_3(\text{CO})_6]^-$

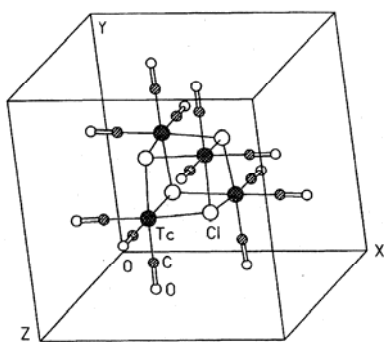


X = Cl: Alberto et al., 1997;

X = Br: Zobl et al., 2008;

X = $\text{OHCH}_2\text{CH}_2\text{S}$: Alberto et al., 1996

Tetramers $[\text{TcX}(\text{CO})_3]_4$



Crystal structure of $[\text{TcCl}(\text{CO})_3]_4$
(body-centered cubic structure,
only the molecule in the cell
center is shown)

Other tetramers (similar
molecular structure):

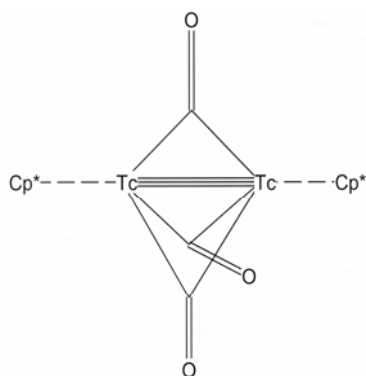
X = OH [Alberto et al., 1998],
tetrahydrate, rhombic

X = (OH,F), rhombic

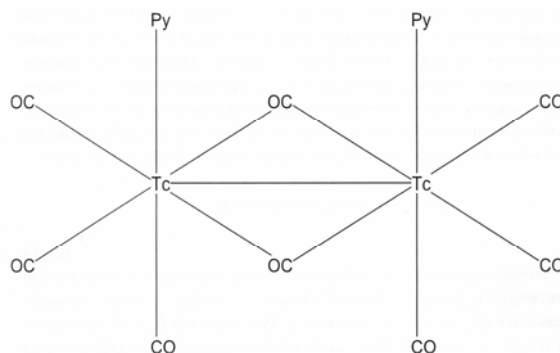
X = I, monoclinic

Mixed tetramer
 $[(\text{MeCN})_2\text{Na}][\text{Tc}(\text{CO})_3]_3(\text{OCH}_3)_4$
[Herrmann et al., 1991]

Complexes with bridging CO groups



Raptis et al., 1991



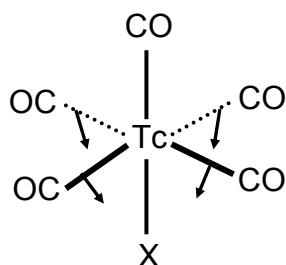
Zuhayra et al., 2008

Tc–CO bond lengths in higher carbonyls, Å (Tc–CO: trans to other ligand; Tc–CO*: trans to CO)

Complex	Tc–CO	Tc–CO*	Difference
$[\text{Tc}(\text{CO})_6]^+$	–	2.024–2.032	–
$\text{TcCl}(\text{CO})_5$	1.915	av. 2.016	0.099
$\text{TcBr}(\text{CO})_5$	1.937	av. 2.021	0.084
$\text{TcI}(\text{CO})_5$	1.938	2.015	0.077
$[\text{Tc}(\text{CO})_5]_2$	1.946	av. 1.998	0.052
$[\text{Tc}(\text{CO})_5(\text{PPh}_3)]^+$	2.005	av. 2.000	0.005
$[\text{Tc}(\text{CO})_5(\text{Bu}^t\text{NC})]^+$	1.999	av. 2.014	–0.014
$[\text{TcI}(\text{CO})_4]_2$	av. 1.91	av. 2.00	0.09
$\text{Tc}(\text{MeOCS}_2)(\text{CO})_4$	av. 1.940	av. 2.008	0.068
$[\text{TcH}(\text{CO})_4]_3$	av. 1.943	av. 2.002	0.059

Reactivity of $\text{TcX}(\text{CO})_5$ in dissociative decarbonylation, series of X:
Cl > Br > I >> $\text{Tc}(\text{CO})_5$, PPh_3 , RNC , CO

Nonclassical interaction in $\text{TcX}(\text{CO})_5$



CO groups "lean" toward X

Average angle X-Tc-cis-CO , deg,
and Wiberg indices $\sum W(\text{X}\cdots\text{C}, \text{X}\cdots\text{O})$

X	Angle (XRD)	Angle (QCC)	$\sum W$
Cl	89.23	86.7	0.24
Br	88.27	86.5	
I	87.8	86.5	0.36

Two kinds of reactivity of Tc carbonyls

(# denotes suggested but not detected intermediates)

- **Dissociative process:**
 $\text{L}_5\text{Tc-CO} \rightarrow [\text{L}_5\text{Tc}]^\# \rightarrow$ dimerization or addition of another ligand

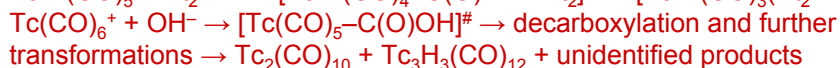
- **Nucleophilic process:**



Dissociative mechanism (relatively slow reactions at room temperature) :



Nucleophilic mechanism suggested (fast reactions at room temperature):



trans-OC-Tc-CO, "long" Tc-CO bond: reactive toward nucleophiles

trans-OC-Tc- σ, π -donor, "short" Tc-CO bond: resistant to nucleophiles
 $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+ + \text{OH}^- \rightarrow$ protolytic transformations, olation, $\text{Tc}(\text{CO})_3$ moiety intact

Comparison of compounds $\text{TcX}(\text{CO})_5$ and $\text{TcX}(\text{CO})_3(\sigma\text{-donor})_2$ (geometries and physicochemical properties)

$\text{TcBr}(\text{CO})_5$: $d(\text{Tc}-\text{Br})$ 2.6123(9) Å (XRD), 2.616 Å (QCC)

$[\text{TcBr}(\text{CO})_3(\text{en})]$: $d(\text{Tc}-\text{Br})$ 2.640(1) Å (XRD)

$\text{TcCl}(\text{CO})_5$: $d(\text{Tc}-\text{Cl})$ 2.4815(19) Å (XRD), 2.478 Å (QCC), $W(\text{Tc}-\text{Cl})$ 0.38

$[\text{TcCl}_3(\text{CO})_3]^-$: $d(\text{Tc}-\text{Cl})$ 2.563 Å (QCC), $W(\text{Tc}-\text{Cl})$ 0.32

$\text{TcX}(\text{CO})_5$ (X = Cl, Br): covalent molecules, noticeably volatile at room temperature, no pronounced tendency to electrolytic dissociation

$[\text{TcBr}(\text{CO})_3(\text{en})]$: sublimes only at $T \approx 200^\circ\text{C}/\text{vacuum}$

$[\text{TcCl}(\text{CO})_3(\text{H}_2\text{O})_2]$: pronounced electrolytic dissociation in aqueous solution, low complexation constants in the system $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+-\text{Cl}^-$

ACKNOWLEDGMENTS

- To International Science and Technology Center and Russian Federation for Basic Research for financial support
- To colleagues who participated in experimental studies and discussions
- To all the attendants for attention