TECHNETIUM(I) HEXACARBONYL CATION AND ITS REACTIVITY

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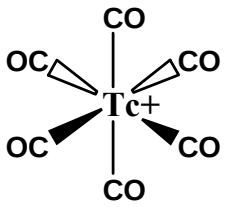
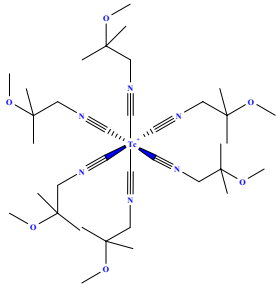
Technetium(I) hexacarbonyl cation $[Tc(CO)_6]^+$ is a an analog of well known heart imaging agent MIBI



technetium(I) hexacarbonyl cation



MIBI

hexakis(2-methoxy-2-methylpropyl-1-isonitrile-technetium(I)

Published procedures for preparing technetium(I) hexacarbonyl

$$Tc(CO)_5Cl + AlCl_3 + CO \xrightarrow[90^oC]{300\ atm} [Tc(CO)_6][AlCl_4]$$

Hieber W., Lux F., Herget C. Uebee Kohlenoxidverbindungen des Technetiums // Z. Naturforsch, 1965, Vol. 20b, P. 1159-1165.

$$[Tc(CO)_3(H_2O)_3]ClO_4 + CO \xrightarrow[50\ atm]{2\ M\ HClO_4} [Tc(CO)_n(H_2O)_{6-n}]^+ \quad n = 0\text{-}3$$

Aebischer N., Schibli R., Alberto R., Merbach A.E. Complete Carbonylation of *fac*-$[Tc(H_2O)_2(CO)_3]^+$ under CO Pressure in Aqueous Media: A Single Sample Story! // Angew. Chem. Int. Ed., 2000, Vol. 39, No. 1, P. 254-256.

$$Mo(CO)_6 \xrightarrow{Neutron\ radiation} [^{99m}Tc(CO)_6]^+$$

Nefedov, V.D. and Mikulai, Stabilization of doughter 99mTc after β-decay of 99Mo in molybdenum hexacarbonyl, Radiochemsitry, 1973, Vol. 15, № 6, P. 846-852

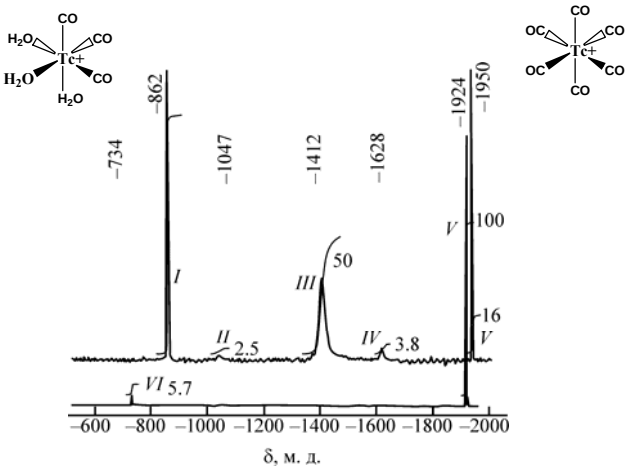
Synthesis of technetium hexacarbonyl

$$[Tc(CO)_3(H_2O)_3]Cl + CO \xrightarrow[2\ M\ HCl,\ 170^oC]{200\ atm} Tc(CO)_5Cl$$

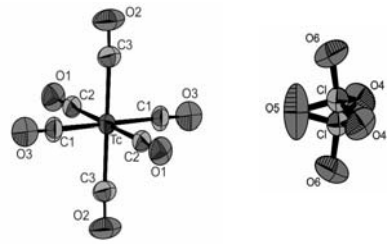
$$[Tc(CO)_3OH]_4 \text{ or } [Tc(CO)_3(H_2O)_3]ClO_4 + CO \xrightarrow[2\ M\ HClO_4,\ 170^oC]{150\ atm} [Tc(CO)_6]ClO_4$$

Autoclave for high-pressure carbonylation

^{99}Tc NMR spectrum of reaction mixture $[Tc(CO)_3OH]_4$ + CO в 2 M $HClO_4$



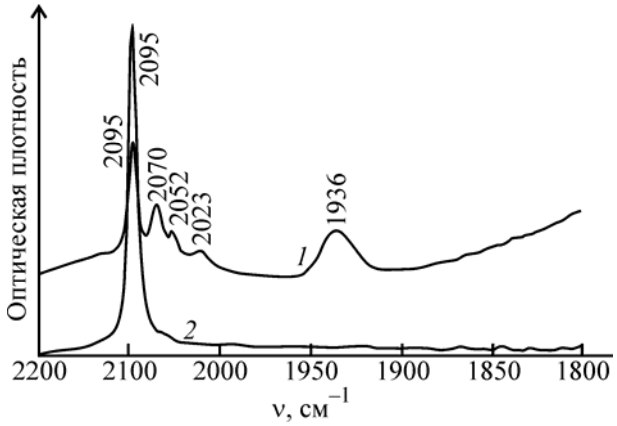
Molecular structure of $[Tc(CO)_6]ClO_4$



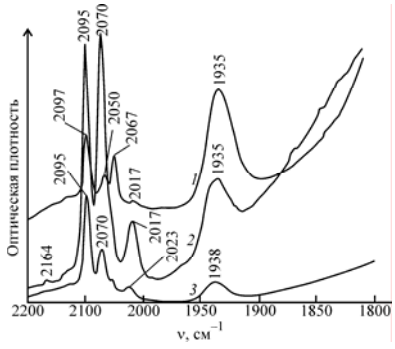
Interatomic distances

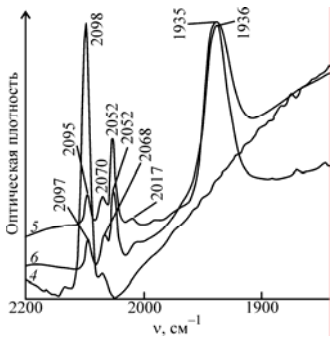
Tc–C1	2.032(3)	C1–O3	1.109(4)
Tc–C2	2.029(3)	C2–O1	1.111(4)
Tc–C3	2.024(3)	C3–O2	1.117(4)
Cl–Cl	0.728(3)	Cl–O5	1.358(6)
Cl–O4	1.393(4)	Cl–O6	1.419(6)
Bond angles			
C1–Tc–C1	180	C2–Tc–C3	91.47(13)
C1–Tc–C2	90.35(12)	C2–Tc–C3	88.53(13)
C1–Tc–C2	89.65(12)	C3–Tc–C3	180
C1–Tc–C3	91.41(14)	O3– C1–Tc	178.2(3)
C1–Tc–C3	88.59(14)	O1– C2–Tc	179.6(3)
C2–Tc–C2	180	O2– C3–Tc	177.3(3)

IR Spectra of (1) reaction mixture $[Tc(CO)_3OH]_4$ + CO in 2 M $HClO_4$ and (2) solution of white crystals of $[Tc(CO)_6]ClO_4$ in acetonitrile

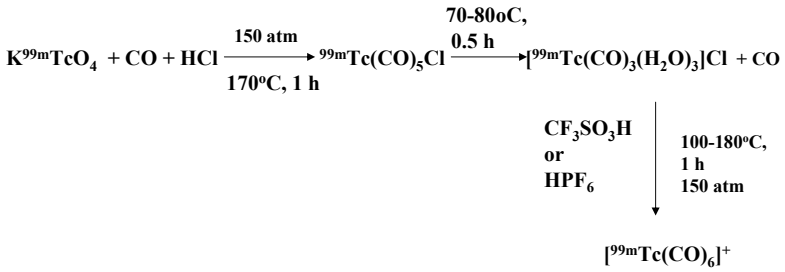


IR spectra of reaction mixtures of $[Tc(CO)_6]^+$ synthesis in 1 – CF_3COOH (2 моль/л, 150 atm CO, 100°C, 10 h), 2 – H_2SO_4 (2 M, 100 atm CO, 200°C, 4 h), 3 – $HOSO_2CF_3$ (2 M, 150 atm CO, 170°C, 1 h), 4 – HPF_6 (2 M, 140 atm CO, 175°C, 1 h), 5 – HF (2 M, 150 atm CO, 175°C, 2 h), 6 – HPF_6 (0.5 M, 110 atm CO, 175°C, 1 h).



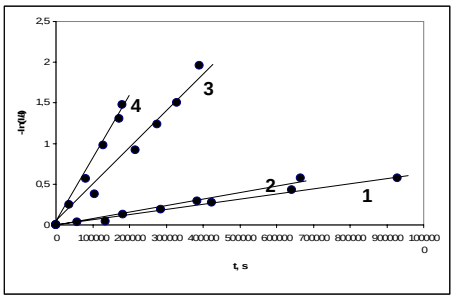


Preparation of $[^{99m}Tc(CO)_6]^+$



Yield of $[^{99m}Tc(CO)_6]^+$ in the presence of triflic acid or HPF_6 is 15 and 40%, respectively.

Kinetics of technetium hexacarbonyl decarbonylation

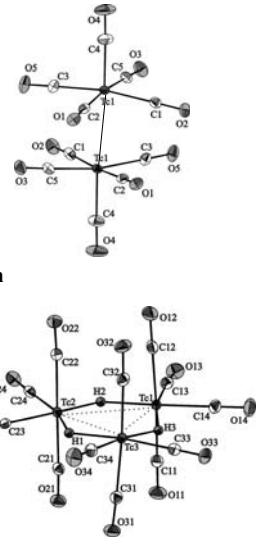


Semilagorithmic anamorphozysis of kinetics curves of hexacarbonyl decrabonylation in acetonitrile at (1) 31.4, (2) 37.1, (3) 44.8 and (4) 48.5°C.

Rate constant of decarbonylation in CH_3CN: $[Tc(CO)_6]^+$ (6.53×10^{-7} s^{-1}, 304.4 K) and $TcBr(CO)_5]$ (2.65×10^{-5} s^{-1}, 303.4 K).

Hydrolysis of technetium hexacarbonyl

$[Tc(CO)_6]^+$ —(alkali, 5 min)→ yellow intermediate —(Vacuum sublimation)→



Conclusions

- Technetium hexacarbonyl perchlorate was prepared and characterized by IR, NMR spectroscopy and SCXRD.
- A procedure for preparing $[^{99m}Tc(CO)_6]^+$ was developed and this carrier free complex was obtained in reasonable yield.
- Technetium(I) hexacarbonyl cation is kinetically stable with respect o thermal decarbonylation in solutions and rapidly decomposes in the presence of strong bases.