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著者	Hashimoto K., Yamada-Maruo Y., Iino S., Omori T., Yoshihara K.
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II. 2. Syntheses of Technetium β -Diketone and 8-Quinolinol Complexes

Hashimoto K., Yamada-Maruo Y.**, Iino S.***, Omori T. and Yoshihara K.*

Department of Chemistry, Faculty of Science, Tohoku University

Together with the development of technetium chemistry in the field of radiopharmaceuticals, its coordination chemistry has been interested in connection with those of molybdenum, ruthenium and rhenium. Systematic studies have substantially been started in the past decade and a variety of complexes have been synthesized and characterized.

In the present paper, syntheses of tris(benzoylacetonato)technetium(III) ($\text{Tc}(\text{bzac})_3$), tris(2-thenoyltrifluoroacetato)technetium(III) ($\text{Tc}(\text{tta})_3$), dichlorobis(8-quinolinolato)technetium(IV) ($\text{TcCl}_2(\text{ox})_2$), chlorobis(acetylacetonato)oxotechnetium(V) ($\text{TcOCl}(\text{acac})_2$), chlorobis(benzoylacetonato)oxotechnetium(V) ($\text{TcOCl}(\text{bzac})_2$) and chlorobis(dibenzoylmethanato)oxotechnetium(V) ($\text{TcOCl}(\text{dbm})_2$), were described. These complexes have not hitherto been synthesized.

Experimental

Ammonium pertechnetate was obtained from the Radiochemical Centre, Amersham. All the reagents used were of guaranteed reagent grade.

Tris(β -diketonato)technetium(III) complexes were synthesized by the method proposed by Abrams et al.¹⁾ $\text{Tc}(\text{bzac})_3$ and $\text{Tc}(\text{tta})_3$ labelled with ^{99}Tc were further purified by alumina and silica gel column chromatography several times in order to eliminate excess ligands. The content of technetium in each complex was determined radiochemically. Anal. for $\text{Tc}(\text{tta})_3$: Calculated for $\text{C}_{24}\text{H}_{12}\text{O}_6\text{F}_9\text{S}_3\text{Tc}$: Tc, 13.0 %; Found: Tc, 13.7 %.

Owing to low yield of $\text{Tc}(\text{bzac})_3$, however, its purity was confirmed by a silica gel column chromatography.

*Present address: Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11.

**Present address: NTT Applied Electronics Laboratories, Nippon Telegraph and Telephone Corporation, Musashino, Tokyo 180.

***Present address: Yamagata 3M Ltd., Higashine, Yamagata 999-37.

$\text{TcCl}_2(\text{ox})_2$ was synthesized by modifying the procedure of Mazzi et al.²⁾ The elemental analysis was done using a CHN corder in the Cyclotron and Radioisotope Center, Tohoku University. Found: C, 47.91; H, 2.48; N, 7.02. Calculated for $\text{TcC}_{18}\text{H}_{12}\text{O}_2\text{N}_2\text{Cl}_2$: C, 47.18; H, 2.64; N, 6.11.

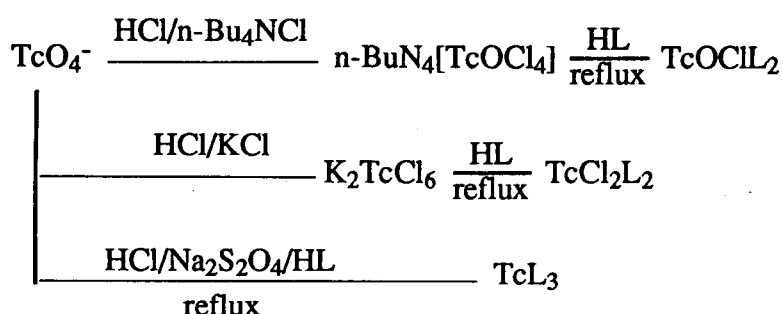
$\text{TcOCl}(\text{acac})_2$ was synthesized as follows: To a methanol solution of 3.1×10^{-4} M tetrabutylammonium tetrachlorooxotechnetate(V) a methanol solution of acetylacetonone (1.9 mmol) was added dropwise. The solution was refluxed for 24 hours. The solvent was evaporated repeatedly and finally black crystals which are almost insoluble in methanol were obtained. The crude materials were recrystallized from chloroform/methanol. At this stage the elemental analysis was performed and formation of the desired complex was confirmed. Geometrical isomers (cis- and trans-forms) were further separated on a silica gel column chromatography using a mixture of 4 % (v/v) diethyl ether-dichloromethane as an eluent. Identification of geometrical isomers was done by means of a proton NMR spectroscopy. An electrochemical method using an ion selective electrode and colorimetric method were employed to determine chloride ion.

Both dibenzoylmethanato and benzoylacetato complexes were synthesized similar to acetylacetonato complex.

Radioactivity of ^{99}Tc was measured with a liquid scintillation counter.

Results and Discussion

Synthetic processes for the technetium complexes for the technetium complexes in various oxidation states have been established fundamentally using pertechnetate as a starting material as follows:



where HL means a bidentate ligand.

Tris(β -diketonato)technetium(III) was obtained in rather low yield by the direct reduction of pertechnetate in the presence of ligand. The final yields were about 30 % for $\text{Tc}(\text{acac})_3$, about 20 % for $\text{Tc}(\text{tta})_3$ and less than 10 % for $\text{Tc}(\text{bzac})_3$ ³⁾. The yield could be improved by using hexakis(thiourea)technetium(III) chloride ($[\text{Tc}(\text{tu})_6]\text{Cl}_3$) as a starting

material. In the presence of excess thiourea, pertechnetate can easily be reduced to Tc(III) and the reddish-orange precipitate of $[\text{Tc}(\text{tu})_6]\text{Cl}_3$ is formed in an hydrochloric acid-ethanol solution. Thus, reflux of an ethanol solution of $[\text{Tc}(\text{tu})_6]\text{Cl}_3$ with a desired β -diketone in the presence of a reducing agent gave tris(β -diketonato)technetium(III) complex in a reasonable yield.⁴⁾ Tris(β -diketonato)technetium(III) coordinated with unsymmetrical ligands possesses geometrical isomers such as mer- and fac-complexes. In the Tc(bzac)₃ complex system, a complete separation of geometrical isomers can be achieved on a silica gel column using a mixture of 1% diethylether and 99% benzene as an eluent. For Tc(tta)₃, however, separation of the isomers is fairly difficult as expected from the adsorption behaviour of tris(β -diketonato)metal(III) complexes.⁵⁾

Geometrical isomers for chlorobis(β -diketonato)oxotechnetium(V) were also separated using a silica gel column. When a mixture of 4%(v/v)diethylether and dichloromethane was employed as an eluent, cis-and trans-complexes could effectively separated, though diethylether was associated strongly with the complex.⁶⁾

Electronic spectral data for newly synthesized complexes are summarized in Table 1.

All of the complexes synthesized are stable even in an acid media.⁴⁾, but these decomposes in an alkaline solution to pertechnetate by the base hydrolysis mechanism.

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Table 1. Electronic spectral data for various technetium complexes in chloroform.

Complex	Absorption maxima*/nm					
Tc(acac) ₃	272 (4.23)	283 ^{sh} (4.19)	347 (4.00)	372 (3.86)	505 (3.65)	533 (3.65)
Tc(tta) ₃		285 ^{sh} (4.32)	332 (4.66)	428 (4.19)	608 (3.96)	660 (4.03)
fac-Tc(bzac) ₃		280 (4.55)	295 (4.54)	390 (3.94)	585 (3.73)	615 (3.74)
mer-Tc(bzac) ₃		280 (4.54)	298 (4.54)	390 (3.99)	585 (3.79)	615 (3.79)
TcCl ₂ (ox) ₂	251 (4.65)			401 (3.83)		
cis-TcOCl(acac) ₂	248 (4.16)	278 (4.12)		408 (4.03)		
trans-TcOCl(acac) ₂ **		272 (4.13)		414 (4.03)		
cis-TcOCl(bzac) ₂ **		283 ^{sh}	303 (4.45)	426 (4.08)		
trans-TcOCl(bzac) ₂ **			300 (4.48)	431 (4.12)		
cis-TcOCl(dbm) ₂ **		277 (4.60)	322 (4.71)	443 (4.35)		
trans-TcOCl(dbm) ₂ **			326 (4.64)	439 (4.23)		

*Molar extinction coefficient (log ε) is in parentheses.

**Measured in 4%(v/v) diethyl ether-dichloromethane.