Coordination Chemistry Reviews, 71 (1986) 389–400
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

7 TECHNETIUM

JANET E. TURP

CONTENTS

Introduction

The period of this review covers those publications in volumes 96 and 97 of Chemical Abstracts. Thus, although the majority of papers covered were published in 1982, many from 1981 are also included. The major journals are covered up to the end of 1982.

The review concentrates upon the coordination chemistry of technetium. No attempt has been made to cover work of an essentially organometallic, catalytic or kinetic nature.

Two publications of general interest to technetium chemists have been published this year: the first discusses the preparation and characterisation of nitrogen-sulfur donor ligands and their technetium complexes [1], and the second describes the preparation and characterisation of several technetium complexes with tetraazamacrocyclic amine ligands for their potential radiopharmaceutical use [2].

0010-8545/86/$4.20

7.1 Technetium(VII)

The first report of a ^{99}Tc NMR spectroscopic study of a technetium complex other than $[TcO_4]^-$ has been reported. ^{99}Tc is the only NMR active technetium isotope (I = 9/2) possessing a significantly long half life. It can be obtained in 100% abundance and has a relative receptivity (compared to ^{1}H) of 0.275. The ranges of ^{99}Tc NMR parameters for d^0 technetium(VII) and d^2 technetium(V) were established. ^{99}Tc and ^{1}H NMR spectroscopic studies have provided definitive evidence for the existence of the stereochemically non-rigid $[TcH_9]^{2-}$ ion. The ^{99}Tc resonance is shifted 3672 ppm to high field of the $[TcO_4]^-$ resonance with a ^{99}Tc–^{1}H coupling of 224 Hz. ^{99}Tc, ^{17}O and ^{19}F NMR spectra were also used to characterise $[TcO_3F]$ and the novel $[TcO_3]^+$ cation. Preliminary results on new technetium(VII) oxofluorides (tentatively identified as $[F_2O_2TcOTcO_2F_2]$ and $[TcO_2F_3]$) were also reported [3].

The facile reduction of technetate(VII) by transition metal "borides" (iron, cobalt and nickel) produced by the reaction of the transition metal halides with sodium borohydride has been investigated and discussed [4]. The extraction of $H[TcO_4]$ has been studied in benzene solutions with acidity ranging from pH 1 to 10 and concentrations of organic oxide (trioctylarsine oxide or trioctylamine oxide) between 0.001 and 0.2 *M*; the extraction isotherms indicated the formation of mono- and di-solvates. The IR spectra of the extractants $[R_3EOH][TcO_4]$ and $[(R_3EO)_2H][TcO_4]$ (E = As or N) were presented and can be seen not to contain water [5].

The reduction of $[NH_4][TcO_4]$ with aminoiminomethane sulfinic acid in the presence of $Na[S_2CNEt_2]$ was found to give the technetium(III) complex $[Tc(S_2CNEt_2)_3(CO)]$ [6,7].

7.2 Technetium(VI)

The catalytic oxidation of plutonium(III) by hydrogen peroxide in nitric acid in the presence of technetium(VI) was studied spectrophotometrically. The reaction orders were found to be 1, 1.4 and 2 in H_2O_2, technetium(VI) and $[H]^+$ respectively. The mechanism was thought to include a rate determining reduction of technetium(VI) by plutonium(III), followed by the rapid oxidation of technetium(V) to $[TcO_2]^{2-}$ by H_2O_2 [8]. The effect of nitric acid and hydrazinium nitrate concentrations, and alkyl chain length, on the formation kinetics and stabilities of technetium xanthate complexes in microemulsions have been studied. The technetium:xanthate ratio in these complexes is 1:6. The IR and electronic spectra of the complex were presented [9].

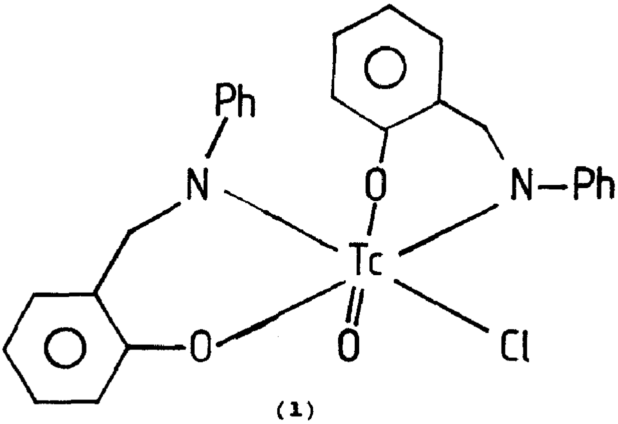
7.3 Technetium(V)

The range of ^{99}Tc NMR spectral parameters of d^2 technetium(V) complexes has been established. The diamagnetic d^2 anion $[TcO_2(CN)_4]^{3-}$ represents the most deshielded ^{99}Tc environment encountered in this first detailed ^{99}Tc NMR spectroscopic study of species other than $[TcO_4]^-$ [3].

The preparation of $[Bu_4N][TcOCl_4]$ has been reported in *Inorganic Synthesis* (technetium chemistry has come of age!). Aqueous $[NH_4][TcO_4]$ is added to hydrochloric acid to give a green solution, to which $[Bu_4N]Cl$ (75% w/w solution) is then added dropwise to precipitate the grey/green $[Bu_4N][TcOCl_4]$. The properties of the compound are also reported [10].

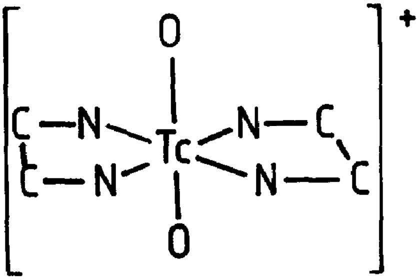
The catalytic oxidation of plutonium(III) by hydrogen peroxide in nitric acid solution in the presence of technetium(VI) has been studied spectrophotometrically. The mechanism was found to include a rate determining reduction of technetium(VI) to technetium(V) by plutonium(III) followed by its rapid oxidation [8].

The olive-green complex $[AsPh_4][TcOCl_4]$ (prepared by bubbling HCl gas through an ethanolic solution of $[Ph_4As][TcO_4]$) was used to synthesise the violet brown $[TcOClL'_2]$: (1), and the deep orange $[Ph_4As][TcOCl_3L']$ (HL' = *N*-phenylsalicylideneimine). The complexes were characterised, and an X-ray crystal structure of (1) showed the crystal to have a monoclinic space group $P2_1/n$, with the technetium in a distorted octahedral environment produced by one oxygen, one chlorine and two chelated L' ligands. The structural parameters were as expected [11].



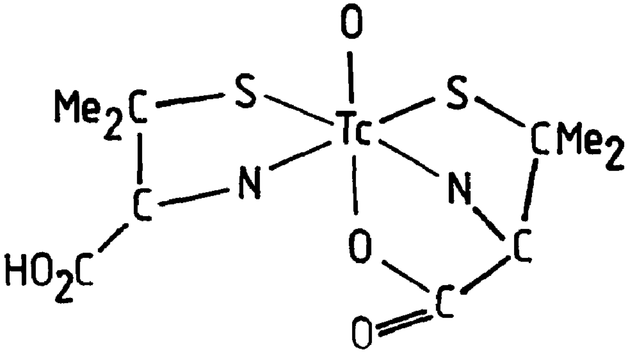
(1)

Addition of 1,2-diaminoethane to a solution of $[Bu_4N][TcOCl_4]$ in tetrahydrofuran until the green colour of the starting material had disappeared yielded the complex *trans*-$[TcO_2(en)_2]^+$; (2), as a brownish orange to pink aggregate. Chromatography isolated an orange-pink product, which was converted to the yellow iodide by allowing a solution of the complex in saturated potassium iodide solution to stand overnight. The crystal structures of the chloride and iodide were determined. The technetium(V) showed octahedral geometry with two *trans* oxo ligands. This unusual configuration (most other oxotechnetium(V) structures are square pyramidal with one apical Tc=O bond) has long Tc=O bonds {r(Tc=O): 0.1746 nm., compared to 0.162–0.165 nm. for monooxo complexes} believed to be due to the pronounced *trans* effect of the oxo ligands, which was also noted for monooxotechnetium(V) complexes. The diamagnetic complex was rapidly hydrolysed in acidic media to yield free 1,2-diaminoethane [12].



(2)

To enable a more complete characterisation of technetium radiopharmaceuticals, 1-oxo-2,3,6-(D-penicillaminato- *N*,*S*,*O*)-4,5-(D-penicillaminato-*N*,*S*)-technetium(V), $[TcO(C_5H_9NO_2S)(C_5H_{10}NO_2S)]$; (3),



(3)

has been synthesised by the addition of D-(−)-penicillamine in water to a solution of $[NH_4][TcOCl_4]$, followed by evaporation to dryness. The crystals were shown to be orthorhombic, space group $P2_12_12_1$; and the technetium was bonded to oxygen {*r*(Tc=O): 0.1657 nm.}, the nitrogen, sulfur and oxygen atoms of a D-penicillaminato dianion deprotonated at sulfur and oxygen, and the nitrogen and sulfur atoms of a D-penicillaminato monoanion deprotonated at sulfur. The Tc–O bond was 0.2214 nm. long, comparable to the Tc–N bonds of 0.2185 nm. and 0.2209 nm. The Tc–S distances were as expected. The molecules were strongly hydrogen-bonded from carboxylic acid to carboxylate ion in a helical chain within the crystal [13].

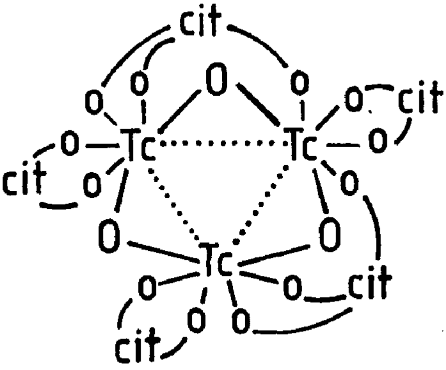
7.4 Technetium(IV)

The luminescence spectra of $[TcCl_6]^{2-}$ in $Cs_2[TeCl_6]$ and of $[TcBr_6]^{2-}$ in $Cs_2[ZrBr_6]$ have been measured at 5 K between 15000 and 3000 cm^{-1}. Five electronic transitions between the states derived from the t_{2g}^3 configuration were observed, each showing extensive vibronic structure. The assignments of the transitions were discussed [14].

$[Ph_4P][TcCl_4(sal)]$ was synthesised from $[Ph_4P]_2[TcCl_6]$ and salicylaldehyde, and was characterised by standard techniques. The crystal structure was determined as monoclinic, with space group $P2_1/c$, and shown to consist of octahedral anions with tetrahedral cations; the equatorial $\{TcCl_2(sal)\}$ unit has approximate planarity [15].

Reactions of $[TcBr_6]^{2-}$ and different substituted and unsubstituted aliphatic carboxylic acids (including tartaric, malic, α-hydroxybutyric, malonic, maleic, succinic, glutaric and aconitic) were studied using spectrophotometric, electrophoretic and chromatographic methods. Unsubstituted di- and tri-carboxylic acids were unable to stabilise technetium(IV) against hydrolysis in these reactions: the products were dark brown precipitates, probably of TcO_2. The hydroxycarboxylic acids were able to replace the bromide ligands to give brown 1:1 polymeric anionic complex ions and low molecular weight red-violet hydroxycarboxylatotechnetates(IV), even with a monohydroxymonocarboxylic acid as ligand. It was thought that the red-violet complexes were mixed hydroxo and/or oxo compounds [16]. The reaction of $Na_2[TcBr_6]$ and citric acid yields a violet polynuclear complex of composition

$Na_9[Tc_3O_3(cit)_5].10H_2O$. It was characterised by chemical, spectral (IR and NMR), magnetic and electrochemical measurements. The effective magnetic moment of 1.2 μ_B is well below the spin only value for a d^3-octahedral centre and is thought to be a result of extensive spin exchange within the trimeric technetium core.

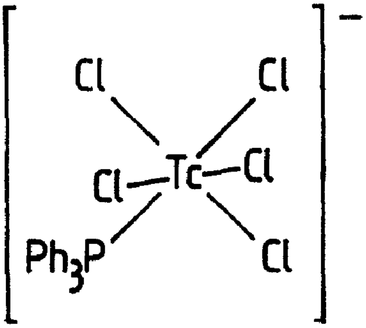


(4)

On the basis of these data, a structure for the complex (4) was proposed [17].

A series of mixed chloro/phosphine technetium(IV) complexes have been synthesised by reaction of $[TcO_4]^-$ with PPh_3 in various concentrations of hydrochloric acid. With concentrated hydrochloric acid, $[TcCl_6]^{2-}$ was obtained and as the hydrochloric acid concentration was decreased, brown-orange $[TcCl_5(PPh_3)]^-$ and yellow $[TcCl_4(PPh_3)_2]$ could be precipitated by the addition of cations such as $[PPh_3H]^+$, $[AsPh_4]^+$ or $[Ph_3PC(Me)_2CH_2COMe]^+$. The crystal structure of (1,1-dimethyl-3-oxobutyl)triphenylphosphonium pentachloro(triphenylphosphino)- technetate(IV): (5), prepared by adding an ethanolic solution of triphenylphosphine to a mixture of $[H_3NC(Me)_2CH_2COMe][TcO_4]$ and hydrochloric acid (37%) (the novel cation being formed by reaction of triphenylphosphine with the original cation), showed well separated units of *pseudo*-octahedral $[TcCl_5(PPh_3)]^-$ anions and *pseudo*-tetrahedral phosphonium cations: {*r*(Tc–Cl) 0.234 nm., *r*(Tc–P) 0.257

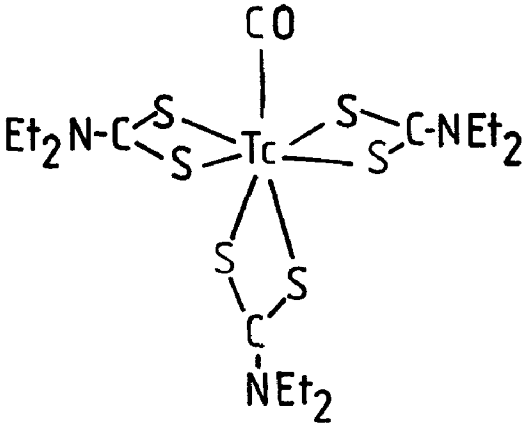
nm.). No intermediate is seen in the reduction of $[TcO_4]^-$ to technetium(IV) by PPh_3, which contrasts with the reduction of $[ReO_4]^-$ in which a Re=O intermediate is observed [18].



(5)

7.5 Technetium(III)

Orange-brown {(carbonyl) tris(diethyldithiocarbamato}technetium(III), $[Tc(S_2CNEt_2)_3(CO)]$: (6), was prepared by the reduction of $[NH_4][TcO_4]$ with aminoiminomethane sulfinic acid in the presence of $Na[S_2CNEt_2]$. The formation of the carbonyl complex was unexpected, but it is of significance to any intended use of the aminoiminomethane sulfinic acid as a reducing agent in the preparation of ^{99m}Tc radiopharmaceuticals. The crystal structure was determined and the complex shown to be isostructural with the rhenium analogue, consisting of discrete $[Tc(S_2CNEt_2)_3(CO)]$ units each containing a linear Tc-C-O group ($Tc-\hat{C}-O$: $178(1)^\circ$).



(6)

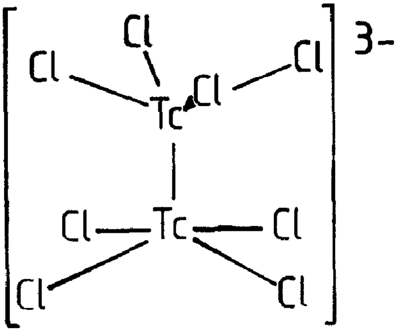
The seven-coordination around the technetium is best described as a distorted pentagonal bipyramid with two of the S_2CNEt_2 ligands occupying equatorial positions and the third spanning an equatorial and an axial site. The formamidine sulfinic acid acts as the source of CO and it is thought that the carbonyl group is formed after $NH_2(NH)CSO_2H$, or some decomposition product, has coordinated to the technetium(III) centre [6,7].

Dihydridochlorobis{1,2-bis(diphenylphosphino)ethane}technetium(III) has been prepared by treating $[TcCl_2L_2]$ (L = dppe) with $Li[AlH_4]$ in thf [19].

7.6 Low Oxidation States of Technetium

The crystal structure of potassium dichlorotetraethanoatoditechnetate(III/II) $K[Tc_2(CH_3COO)_4Cl_2]$ shows that each technetium is octahedrally coordinated by one technetium atom, four oxygen atoms and one chlorine atom. The four ethanoate groups act as bridging bidentate ligands [20]. The crystal structure of $[Tc_2(CH_3COO)_4]Cl$ has also been determined. It consists of chloride ions acting as bidentate bridges between $\{Tc_2(CH_3COO)_4\}^+$ cations. These cations consist of two technetium atoms with a bond order of 3.5, linked by four bridging bidentate ethanoate groups [21].

The crystal structure of yttrium octachloroditechnate(III/II) nonahydrate shows that the molecule contains equal numbers of $[Tc_2Cl_8]^{3-}$ ions; (7), at sites of C_4 symmetry and slightly distorted square antiprismatic $[Y(H_2O)_8]^{3+}$ ions on sites of D_2 symmetry [22].



(7)

The shortness of the Tc–Tc bond (0.2108 nm.: bond order 3.5) when compared to that in $[Tc_2Cl_8]^{2-}$ (0.2151 nm., [23]), where the formal bond order of four is higher, is attributed mainly to the decreased effective positive charge on the metal atoms in the 3- ion, which leads to stronger π-bonding [22].

There has been a charge overlap study of multiple metal-metal bonding and conjugation in linear chains of transition metal atoms including technetium [24].

Room temperature EPR spectra of the paramagnetic low spin d^5 technetium cation *trans*-aquanitrosyltetraamminetechnetium(II); (8), and anion nitrosylpentachlorotechnetate(II); (9), have been obtained. $[Tc(NH_3)_4(NO)(H_2O)]^{2+}$ was oxidised using $K_2[Cr_2O_7]$ or cerium(IV) sulphate to give an EPR spectrum of (8) with ten lines. On warming in concentrated hydrochloric acid the spectrum changed and the new species was $[Tc(NO)Cl_5]^{2-}$,(9). The *g*-factors are shown in the table 7.1.

Table 7.1 EPR parameters for (8) and (9)

	(8) $[Tc(NH_3)_4(NO)(H_2O)]^{3+}$	(9) $[Tc(NO)Cl_5]^{2-}$
$g_{\parallel}$	1.861±0.039	1.891±0.038
$g_{\perp}$	2.114±0.030	2.104±0.022
$A_{\parallel}$/G	296.6±4.0	281.0±4.0
$A_{\perp}$/G	108.8±5.0	109.3±5.0
g_{iso}	2.026±0.001	2.024±0.001
A_{iso}/G	165.4±1.3	159.4±1.4

The relative closeness of perpendicular and parallel *g*-factors can be accounted for by assuming that the magnitude of tetragonal distortion is much smaller than that of the spin-orbit coupling [25].

$[(PPh_3)_2Tc(CO)_3Cl]$ has exhibited moderate catalytic activity in the metathesis of 2-pentene to 2-butene and 3-hexene. The effects of temperature, time and Tc:substrate ratio were determined [26].

References

1 R.F. Dannals, *Diss. Abstr. Int. B*, 42 (1981) 1009

2 J. Simon, *Diss. Abstr. Int. B*,42 (1981) 645

3 K.J. Franklin, C.J.L. Lock, B.G. Sayer and G.J. Schrobilgen, *J. Amer. Chem. Soc.*, 104 (1982) 5303

4 P.M. Pojer and R.J. Spokas, *Nucl. Med. Commun.*, 3 (1982) 143

5 A.M. Rozen, A.S. Skotnikov and E.G. Teterin, *Zh. Neorg. Khim.*, 27 (1982) 739 (*Chem. Abstr.*, 96 (1982) 206282)

6 J. Baldas, J. Bonnyman, P.M. Pojer, G.A. Williams and M.F. Mackay, *J. Chem. Soc., Dalton Trans.*, (1982) 451

7 J. Baldas, J. Bonnyman, P.M. Pojer and G.A. Williams, *Aust. Radiat. Lab.*

[Tech. Rep.], ARL/TR 1981 ARL/TR 038
8 Yu.P. Susrov, L.M. Ramazanov and V.A. Rorovinskii, *Radiokhimiya*, 23 (1981) 721
9 I.V. Vinogradov, I.V. Shilin, S.V. Shepel'kov and L.S. Sudakova, *Zh. Neorg. Khim.*, 27 (1982) 2003 (*Chem. Abstr.*, 97 (1982) 169938)
10 A. Davison, H.S. Trop, B.V. Depamphilis and A.G. Jones, *Inorg. Synth.*, XXI (1982) 160
11 G. Bandoli, U. Mazzi, D.A. Clemente and E. Roncari, *J. Chem. Soc., Dalton Trans.*, (1982) 2455
12 M.E. Kastner, M.J. Lindsay and M.J. Clark, *Inorg. Chem.*, 21 (1982) 2037
13 K.J. Frankin, M.E. Howard-Lock and C.J.L. Lock, *Inorg. Chem.*, 21 (1982) 1941
14 C.D. Flint and P. Lang, *J. Luminescence*, 24/28 (1981) 301
15 U. Mazzi, E. Roncari and G. Bandoli, *Transition Met. Chem. (Weinheim Ger.)*, 7 (1982) 163
16 B. Grossman and R. Muenze, *Int. J. Appl. Radiat. Isot.*, 33 (1982) 189
17 R. Muenze, *Radiochem. Radioanal. Lett.*, 48 (1981) 281
18 G. Bandoli, D.A. Clemente, U. Mazzi and E. Roncari, *J. Chem. Soc., Dalton Trans.*, (1982) 1381
19 L. Kaden, B. Lorenz, K. Schmidt, H. Sprinz and M. Wachren, *Z. Chem.*, 21 (1981) 232
20 P.A. Kozmin, T.B. Larina and M.D. Surazhskaya, *Koord. Khim.*, 8 (1982) 851 (*Chem. Abstr.*, 97 (1982) 047702)
21 P.A. Koz'min, T.B. Larina and M.D. Surazhskaya, *Koord. Khim.*, 8 (1982) 1719 (*Chem. Abstr.*, 96 (1982) 13966)
22 F.A. Cotton, A. Davison, V.W. Day, M.F. Fredrich, C. Orvig and R. Swanson, *Inorg. Chem.*, 21 (1982) 1211
23 *e.g.* F.A. Cotton and L.W. Shive, *Inorg. Chem.*, 14 (1975) 2032
24 Y-N. Chiu and F.E. Wang, *Inorg. Chem.*, 21 (1982) 4264
25 G.C. Yang, M.W. Heitzmann, L.A. Ford and W.R. Benson, *Inorg. Chem.*, 21 (1982) 3242
26 B. Lorenz, H. Rommel and M. Wehren, *Z. Chem.*, 22 (1982) 224