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6. TECHNETIUM

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CONTENTS

INTRODUCTION

The period of this review covers those publications in volumes 94 and 95 of Chemical Abstracts. Thus, although a majority of papers covered were published in 1981, many from 1980 are also included. The major journals are covered up to the end of 1981.

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.

6.1 TECHNETIUM(VII)

An alternative method for the reduction of pertechnate, without forming the classical technetium-tin radiopharmaceuticals, has been formulated. It involves the addition of ethylenediphosphinetetraacetic (edptaH$_4$) and phosphinetriacetic (ptaH$_3$) acids to $[TcO_4]^-$ eluate to form various types of technetium complexes depending on the Tc:acid ratio. It was shown that in acid media edpta and pta reduce pertechnate [1].

$[TcO_3XL]$ (L = bipy, X = Cl or Br; L = phen, X = Cl) complexes have been prepared by dissolving $[TcO_4]^-$ in ethanol and then treating the solution with L, followed by the slow addition of HX; they were characterised by optical and vibrational spectroscopy. The isolation of these technetium(VII) complexes with poorly reducing ligands may suggest that similar heptavalent species may be

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intermediates in the reactions of $[TcO_4]^-$ in acidic conditions with other ligands which lead to the preparation of complexes in lower oxidation states [2].

6.2 TECHNETIUM(V)

6.2.1 Oxohalides

$[Bu_4N][TcOCl_4]$ and $[Bu_4N][TcOBr_4]$ were prepared by the treatment of $[Bu_4N][TcO_4]$ with concentrated hydrochloric and hydrobromic acids, respectively, at room temperature. Their vibrational spectra indicate C_{4v} symmetry for the anion. An unusual resonance Raman effect is seen in $[Bu_4N][TcOBr_4]$ [3]. $[Bu_4N][TcOI_4]$ was prepared from $[Bu_4N][TcOCl_4]$ by ligand exchange with NaI in propanone. Vibrational spectra again indicate C_{4v} symmetry for the anion and the resonance Raman spectrum shows ν(TcO) at 996 cm^{-1} and four of its overtones, symmetrically surrounded by other sum and difference bands [4].

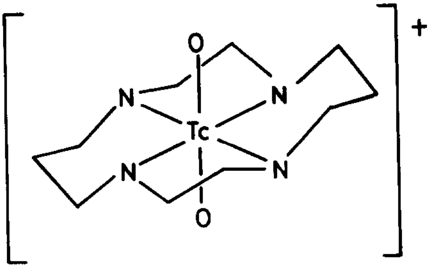
The electroreduction of the oxopentachloro complex of technetium(V), $[TcOCl_5]^{2-}$, has been studied in 4 *M* hydrochloric solution by simultaneous coulometry and spectrophotometry. The UV spectra observed during the reduction of $[TcOCl_5]^{2-}$ show the coexistance of three species; firstly $[TcOCl_5]^{2-}$ (λ_{max} = 228, 294 nm), secondly an intermediate (λ_{max} = 238, 325 nm) shown to be $[Tc(OH_2)Cl_5]^-$ by comparison with other spectra, and thirdly $[TcCl_6]^{2-}$ (λ_{max} = 240, 308, 338 nm). The reduction was shown to be one electron and a kinetic scheme proposed for it [5].

$[TcOX_3(bipy)]$ (X = Cl or Br) has been synthesised from $[Bu_4N][TcOX_4]$ and bipy in an ethanolic solution of aqueous HX [2].

6.2.2 Oxides and complexes with oxygen donor ligands

A review has been published, containing twenty references, on the electronic structure and symmetry of technetium(V) oxy-complexes containing $[TcO]^{3+}$ and $[TcO_2]^+$ groups, on the basis of IR, UV-VIS and X-ray spectroscopic data [6].

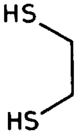
$[TcO_2(cyclam)][ClO_4].H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) was prepared by adding $Na_2[S_2O_4]$ to a solution of $[NH_4][TcO_4]$ and cyclam in a hydrogencarbonate buffer at pH 11. The crystal structure of the product shows a *trans*-dioxo configuration (*1*), the first such technetium(V) complex to be synthesised. The Tc–O bond length {1.751(4) Å} is longer than in a mono-oxo complex and it was postulated that dioxo complexes of technetium(V) are formed when the ancillary ligands are neutral and serve as poor π-donors. The Tc-N distances {2.125(11) Å} are the longest observed yet for any cyclam complex [7].



(1)

6.2.3 Complexes with sulphur donor ligands

A series of ten bis[(dithiolato)oxotechnetate(V)] complexes were prepared from technetium(V) gluconate by ligand exchange. The technetium(V) gluconate complex in aqueous or aqueous ethanolic solution was completely converted into a dithiolato complex by addition of two mole equivalents of the dithiol. The red-yellow products were isolated as tetraethylammonium salts; the ligands used are shown in (*2*) - (*9*). A mixed sulphur-selenium complex was made from (*10*) [8].



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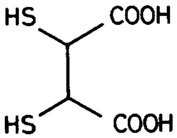

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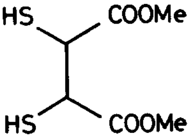

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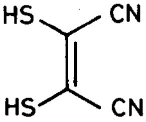

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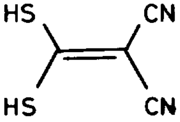

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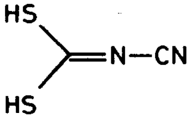

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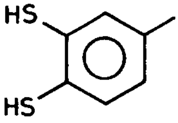

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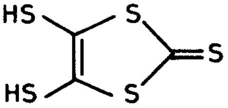

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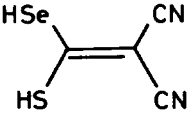
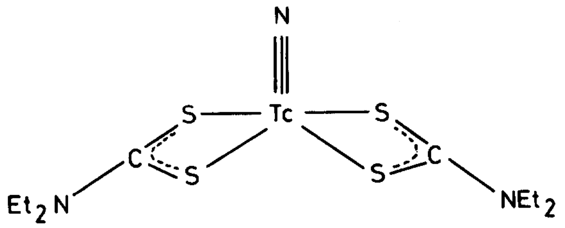


(10)

$[AsPh_4][TcO(SCH_2CH_2O)_2]$ was prepared by adding β-mercaptoethanol to $[NH_4][TcO_4]$, followed by dropwise addition of $Na_2[S_2O_4]$ in 2*M* NaOH solution and precipitation of the pink crystals by addition of $[Ph_4As]Cl$. The crystal structure was determined and the anion found to be approximately square pyramidal. The basal plane is distorted towards a trapezoid because of the difference in the Tc–O {1.950(4) Å} and the Tc–S {2.291(2) Å} distances [9]. The sodium dithionite reduction of $[TcO_4]^-$ in the presence of the benzoyl protected dimercaptodiamides $[\{PhCOS(CH_2)_nC(O)NH\}_2X]$ $\{n = 1, X = (CH_2)_2, (CH_2)_3$ or $1,2\text{-}C_6H_4$; $n = 2$, $X = (CH_2)_2\}$ gives the corresponding technetium(V) anion $[TcO\{S(CH_2)_nC(O)NXNC(O)(CH_2)_nS\}]^-$. The complexes were characterised by field desorption mass spectrometry and IR spectroscopy [10]. Bis(diethyldithiocarbamato)nitridotechnetium(V) $[TcN(S_2CNEt_2)_2]$ (*11*) was prepared by the reduction of $[NH_4][TcO_4]$ with hydrazine in hydrochloric acid, followed by reaction with sodiumdiethyldithiocarbamate in water, after adjustment to pH7.0. The crystal structure showed the yellow crystals to be isostructural with its rhenium analogue. The technetium atom has a distorted square pyramidal envonment with the nitrogen in the apical position, and the four sulphur atoms forming the base $\{r(TcN) = 1.604(6)$ Å$\}$ [11,12].



(*11*)

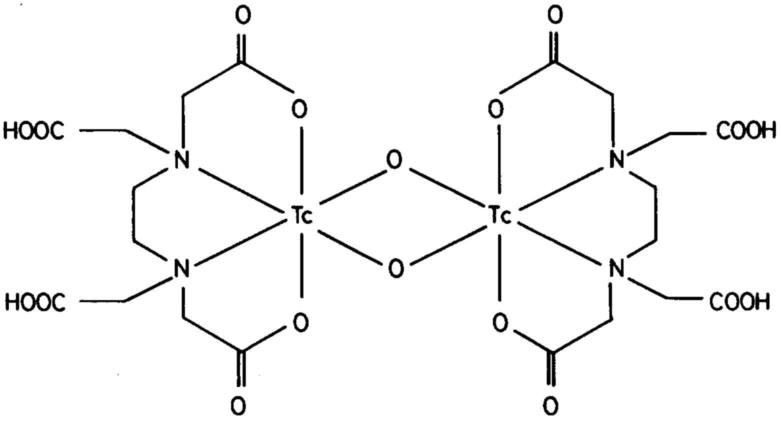
6.2.4 *Complexes with Group VB donor ligands*

Aqueous $[N_2H_6]Cl_2$ treated with PPh_3 in ethanol, reacts with $[NH_4][TcO_4]$ in 0.5 *M* HCl, under argon, with heating, to give $[TcNCl_2(PPh_3)_2]$. Ligand exchange reactions of this compound gave $[TcN(S_2CNEt_2)_2]$, $[TcNCl_2(PMe_2Ph)_3]$ and $[TcNCl_2(PEt_2Ph)_3]$. [13]. $[Ph_4As]_2[OTc(NCS)_5]$ was prepared by dissolving $[Bu_4N][TcOCl_4]$ in methanol and adding $[NH_4][SCN]$, followed by precipitation to give red crystals. This product could react with further $[NCS]^-$ to give a mixture of $[Tc(NCS)_6]^{2-}$ and $[Tc(NCS)_6]^{3-}$ [14].

6.3 TECHNETIUM (IV)

Dinitrogen was found to be reduced to NH_3 by the reaction of $[TcCl_4(PPh_3)_2]$ with lithium napthalene in THF [13].

$[(H_2edta)Tc(\mu\text{-}O)_2Tc(H_2edta)]$ (*12*) was synthesised by mixing $Na_2[H_2edta]$ with one mole equivalent of $H[TcO_4]$ in water followed by addition of an excess of $Na[HSO_3]$. The crystal structure of the complex shows an almost planar four-membered $Tc(\mu\text{-}O)_2Tc$ ring. The Tc-Tc distance (2.33 Å) is between that expected for double and triple bonding, but extended Hückel calculations indicated that the electronic configuration of the triple bond would be $\sigma^2\pi\delta^{*2}$, apparently accounting for the extended M-M bond which was observed.



(*12*)

Technetium(IV) was found to complex with di-(2-ethylhexyl) phosphonic acid (dehpH) and the formation of the complex was studied by the distribution method as a function of pH. The extracted species was [TcO(dehp)(OH)(Hdehp)] [16].

$[TcO_4]^-$ was reduced under acid conditions with the tin(II) complexes of 2-thioacetic acid, 2-thiopropanoic acid and 2-thio-2-methylpropanoic acid. By the use of paper electrophoresis, two complexes were detected and these were postulated as being the 1:1 and 2:1 adducts [17]. $[Tc(NCS)_6]^{2-}$ was observed as one of the products of the reduction of $[TcO(NCS)_5]^{2-}$ with $[SCN]^-$ [14].

6.4 TECHNETIUM(III)

The crystal structure of $[Bu_4N]_2[Tc_2Cl_8]$ has been determined, and the salt is isomorphous with its rhenium analogue. There is disorder in the crystal, with

31% of the $[Tc_2Cl_8]^{2-}$ ions orientated perpendicular to the majority. The average Tc-Tc distance (2.147 Å) is longer than was anticipated [18].

$[Tc_2Cl_2(O_2CMe)_4]$ was prepared by reacting $K[TcO_4]$, HCl and MeCOOH under dihydrogen, and shown by single crystal studies to be isostructural with $[Re_2Cl_2(O_2CMe)_4]$ [19]. $[Tc(NCS)_6]^{3-}$ was obtained as one of the products of the reduction of $[TcO(NCS)_5]^{2-}$ with $[SCN]^-$ [14].

Technetium(III) species were formed by the two-electron oxidation of $[TcCl(CO)_2(PMe_2Ph)_3]$ and $[TcCl(CO)_3(PMe_2Ph)_2]$ in ethanenitrile. Specifically, $[TcCl(CO)(MeCN)(PMe_2Ph)_3][ClO_4]_2$ and $[TcCl_3(CO)_2(PMe_2Ph)_2]$ were isolated and the electrode mechanisms leading to their formation discussed [20]. The electrochemistry of the *trans*-octahedral technetium(III) complexes $[Tc(L\text{-}L)_2X_2)^+$ (L-L = diars or dppe; X = Cl, Br or I) was investigated using OTTLE techniques. All the complexes exhibited reversible Tc(III)/Tc(II) couples in dmf {X = Cl, L-L = dppe; E^o = -0.04 V: X = Cl, L-L = diars; E^o = -0.091 V (*vs.*NaSCE)}. The couples are sensitive to both L-L and X (*i.e.* dppe stabilises technetium(II) relative to technetium(III) to a greater extent than does diars) [21].

6.5 LOW OXIDATION STATES OF TECHNETIUM

$K_3[Tc_2Cl_8].2H_2O$ reacted with MeCOOH in an autoclave at 30-50 atmospheres of argon to give $K[Tc_2(O_2CMe)_4Cl_2]$ and $[Tc_2(O_2CMe)_4Cl]$ the former being claimed to contain two chloro-bridges, and the latter one [22].

X-ray powder diffraction studies were used to determine the structure of $[Tc(CO)_5X]$ (X = Cl or Br). The crystals were found to be orthorhombic with space group *Pnma* and *Z* = 4 [23]. The oxidation of $[TcCl(CO)_2(PMe_2Ph)_3]$ and $[TcCl(CO)_3(PMe_2Ph)_2]$ was studied in MeCN; both complexes underwent an overall two electron oxidation to give technetium(III) species (see Section 6.4) [20].

$[MnTc(CO)_{10}]$ and $[TcRe(CO)_{10}]$ have been synthesised. The Mn-Tc species was prepared by firstly forming $[Mn(CO)_5]^-$ and treating this with $[Tc(CO)_5Br]$ in thf, which was added slowly. The Re-Tc species was formed in a similar manner, using $[Tc(CO)_5]^-$ and $[Re(CO)_5Br]$. These reactions illustrate the general principle of using the weakest nucleophile with the corresponding bromide [24]. The experimental and literature data for the thermodynamic parameters of formation, phase transitions and dissociation of $[Tc_2(CO)_{10}]$ have been discussed, sets of the best values proposed, and the Tc-Tc bond energy determined [25].

The IR spectrum, and its complete assignment on the basis of the free rotational model, of the bimetallic carbonyl $[TcCo(CO)_9]$ was reported. The results show a considerable polarisation of the M-M bond in the sense $\overset{\delta+}{Tc}\text{-}\overset{\delta-}{Co}$ [26].

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