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3 TECHNETIUM

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CONTENTS

INTRODUCTION

The period of this review covers those publications in volumes 98 and 99 of Chemical Abstracts. Thus, although the majority of papers covered were published in 1983, many from 1982 are also included. The major journals (*J. Chem. Soc., Dalton Trans., J. Chem. Soc., Chem. Commun., Inorg. Chem.* and *J. Am. Chem. Soc.*) are covered up to the end of 1983.

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.

Six publications of general interest to technetium chemists have been published this year: the first is a review with 143 references on the chemistry of technetium and rhenium [1]. Another review with 308 references on

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the chemistry of the twelve transition elements in groups 4, 5, 6 and 7, including technetium, has been published [2]. The synthesis, reactivity and molecular structure of technetium in oxidation states (I) - (IV) were reviewed, and the results showed that the technetium(III) state had a diverse chemistry and was accessible from $[TcO_4]$ in aqueous solution. The advancement of the chemistry of technetium(I) with π-acceptor ligands was noted; the review has 104 references [3]. A review has also been written on the electrochemistry of technetium over the period 1973-1980, and topics discussed include various electrochemical techniques, non-aqueous systems, chemical reduction-oxidation reactions and substitution reactions. The review has 34 references [4]. The coordination chemistry of technetium as related to nuclear medicine was reviewed, with 31 references [5], and an investigation of technetium complexes containing bidentate arsine and phosphine ligands and their applications to nuclear medicine was undertaken [6].

3.1 TECHNETIUM(VII)

The temperature dependence of the spin-spin (R_2) and spin-lattice (R_1) relaxation rates of the quadrupolar technetium nucleus in $[TcO_4]$ was studied, and it was deduced that, as there is a minimum in the variation of R_1 and R with temperature in $[TcO_4]$, the lifetime of the excited vibrational state is probably less than the correlation time of orientational motion of the complex [7].

The formation of complexes of ^{99}Tc in oxidation states (VII), (V), (IV) and (III) with edta, dtpa (diethylenetriaminepentaacetate), ada (*N*-(2-acetamido)iminodiacetate) and hida (*N*-(2,6-dimethylphenylcarbamoyl-methyl)iminodiacetate) was studied by various polarographic, coulometric and amperometric techniques, and the natures of the products considered with respect to the reaction conditions [8].

In tripolyphosphate solution, the products of the electroreduction of

$[TcO_4]$ were shown to be pH dependent, with predominantly technetium(III) formed below pH 7, and both technetium(III) and (IV) being formed above pH 7. The electrochemistry and solution chemistry of the Tc(III)/Tc(IV) couple have been studied [9].

The sodium salt $Na_2[\{N(CH_2COO)_3\}^{99}Tc(\mu\text{-}O)_2{}^{99}Tc\{N(CH_2COO)_3\}].6H_2O$ and its potassium analogue were prepared from aqueous solutions of $[^{99}TcO_4]^-$ at ca pH 2, using sulfur dioxide as a reducing agent (see Section 3.4) [10].

The preparation of a number of cationic complexes of technetium(V) with nitrogen-containing ligands was reported, one method involving the reduction of $[^{99m}TcO_4]$ with tin(II) chloride in the presence of an excess of the ligand. The pH dependence of this route was studied, and the results of the reaction monitored by electrophoresis [11].

In the absence of a complexing ligand, technetate(VII) was reduced electrochemically to technetate(VI), and changes in solvent and supporting electrolyte led to variations in the reduction potential. In the presence of 8-hydroxyquinoline, reduction to technetium(IV) occurred with all solvents and electrolytes except $[NBu_4]I$. An explanation of this was presented [12].

3.2 TECHNETIUM(VI)

Tris(2-aminobenzenethiolato(2-)-*S*,*N*)technetium(VI) was prepared from 2-aminobenzenethiol and ammonium technetate(VII), and the crystal structure determined by X-ray diffraction methods (see Fig.1). The unit cell was orthorhombic, space group $P2_12_12_1$, and the compound, which was found to be isostructural with the molybdenum analogue, shown to consist of discrete $[Tc(NHC_6H_4S)_3]$ molecules with apparent trigonal prismatic geometry. The structure was discussed and compared to that of the molybdenum analogue [13].

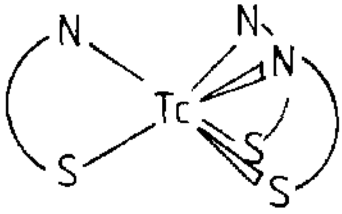

Fig.1: $[Tc(NHC_6H_4S)_3]$

Reduction of $[TcO_4]^{2-}$ by $SnCl_2$ in the presence of an excess of the ligand HL (HL = 1,1-diethyl-, piperidino- or morpholino- 3-benzoylthiourea) yielded the air-stable technetium(III) complexes $[TcL_3]$ [14].

3.3 TECHNETIUM(V)

The synthesis, reactivity and molecular structure of a variety of technetium(V) complexes were reviewed. The oxotechnetium(V) species were most conveniently characterised on the basis of their Tc-O cores: $\{TcO\}^{3+}$, *trans*-$\{TcO_2\}^+$ and linear $\{Tc_2O_3\}^{4+}$. All contained a terminal Tc=O group and were spin-paired, diamagnetic compounds. The complexes TcF_5, $K[TcF_6]$ and $[Tc(diars)_2Cl_4]^+$, which do not contain an oxotechnetium core, were also discussed. The review has 41 references [15].

The electronic spectra of the technetium(V) imidazole complex $[TcO_2(imidH)_4]^+$ were studied by the SCF-X -SW method and the three bands assigned [16]. The ligand exchange reactions of various oxotechnetium(V) complexes with 1,2-dithiols have been investigated. The complex anions $[TcO(L)_2]^-$ (LH_2 = L^1H_2, ethane-1,2-diol; L^2H_2, benzene-1,2-diol; L^3H_2, ethane-1-ol-2-thiol) reacted with ethane-1,2-dithiolate, $[L^4]^{2-}$, to yield $[TcO(L^4)_2]^-$, but different mechanisms or intermediates have been observed in each case. In the reaction of $[TcO(L^3)_2]^-$, an intermediate of the general form $[(TcO)_2(L)_3]$ was identified by electronic spectroscopy. The relation of these results to those for the ligand exchange reaction with citrates was discussed. Furthermore, the reaction of propane-1,3-dithiol with $[TcOCl_4]^-$ yielded the dimer $[(TcO)_2(SCH_2CH_2CH_2S)_3]$ which did not react with more ligand to form the monomer, in contrast to the reaction of the oxochloro species with ethane-1,2-dithiol [17].

The preparation was described of the complex salt oxotetrakis(tetramethylthiourea)technetium(V) hexafluorophosphate, which was used as a convenient starting material for the preparation of the salts hexakis(*N,N'*-dimethylthiourea)technetium(III) hexafluorophosphate, *trans*-dioxotetrapyridinetechnetium(V) hexafluorophosphate and tetraphenylarsonium oxo(*N,N'*-ethylenebis(2-mercaptoacetimido)technetate(V). IR and electronic spectra, conductivity and magnetic moment data were reported for the first two complexes. The last two complexes were compared with authentic samples [18]. In the presence of dioxygen, $[Tc_2Cl_8]^{3-}$ in hydrochloric acid solution formed $[Tc_2Cl_8O_2]^{3-}$ which decomposed to form the technetium(IV) species $[TcCl_6]^{2-}$ and the technetium(V) complex $[Tc(OH)OCl_4]^{2-}$ [19].

The technetium(V) complexes $M_2[TcOCl_5]$ (M = K or Cs) and $Cs_2[TcOBr_5]$ were prepared and the crystal unit cell dimensions of the caesium salts determined [20]. The formation of ^{99}Tc complexes in the +5 oxidation state of edta, dtpa, ada and hida (see section 3.1) was studied by various techniques and the natures of the products discussed with reference to reaction conditions [8].

The preparation of a number of cationic technetium(V) complexes with nitrogen-donor ligands was studied. Of the two methods used, ligand exchange reactions involving technetium(V) hydroxycarboxylates gave the required products in high yield, and the optimum reagents and conditions were discussed. Reduction with tin(II) chloride of $[^{99m}TcO_4]^-$ in the presence of an excess of the ligand also yielded the desired complexes, and the pH dependence of this route was considered. Electrophoresis results were studied. The ligands used included 1,2-diaminoethane, 1,2-bis(dimethylamino)ethane, pyridine, 2,2'-bipyridine, 1,10-phenanthroline, 8-hydroxyquinoline, 2-aminopyridine, nicotinamide, thymine, cytosine, the drugs: sulfisomidine, aminophenazone, *d,l*-ephedrine-HCl and urotropine, and the aminoacids: lysine, histidine and ornithine [11].

A study of the reaction of $[TcOCl_4]^-$ with catechol, LH_2, in methanol showed that a complex of 1:2 stoichiometry was produced, as suggested by the equation:

$$[TcOCl_4]^- + 2LH_2 \rightleftharpoons [TcOL_2] + 4HCl$$

The reaction was monitored by electrophoresis [21].

3.4 TECHNETIUM(IV)

The salt $Na_2[\{N(CH_2COO)_3\}^{IV}Tc(\mu\text{-}O)_2{}^{IV}Tc\{N(CH_2COO)_3\}].6H_2O$, and its potassium analogue, were prepared by reducing a technetate(VII) solution at pH 2 with sulfur dioxide. The X-ray crystal structure of the sodium salt was determined (see Fig.2), and showed that each technetium atom was coordinated to one tetradentate $(N(CH_2COO)_3)^{3-}$ ligand, with two such groups bridged by two oxygen atoms. Evidence for a Tc-Tc interaction was noted. Electronic and ^1H NMR spectral, magnetic and analytical data were presented and discussed [10].

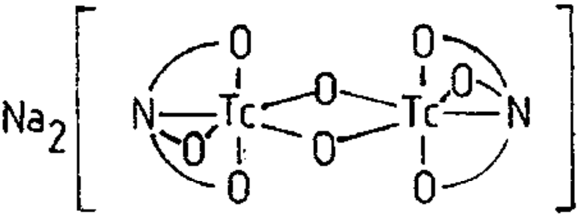

Fig.2: $Na_2[\{N(CH_2COO)_3\}{}^{99}Tc(\mu\text{-}O)_2{}^{99}Tc\{N(CH_2COO)_3\}].6H_2O$

Complexes of technetium with $edtaH_4$ and $dtpaH_5$ (diethylenetriamine pentaethanoic acid) were prepared by ligand exchange with $K_2[TcBr_6]$ in aqueous solution. Spectral and physical data indicated that the products are 1:1 complexes with the formulae $H_2[TcO(dtpa)].2H_2O$, $M_4H_2[Tc_2O(OH)_2(dtpa)_2].4H_2O$ (M = K or $[NH_4]$) and $H_3[TcO(edta)].3H_2O$, and each ligand was reported to coordinate through only two ethanoato groups [22].

The technetium(IV) salts $M_2[Tc(OH)Cl_5]$ (M = K, Rb or Cs) and $Cs_2[Tc(OH)Br_5]$ were prepared using HI as a reducing agent. Electronic and IR spectral, magnetic and crystal unit cell data were presented, and some chemistry of the complexes was discussed [20].

It was reported that, in the presence of dioxygen, $[Tc_2Cl_8]^{2-}$ in hydrochloric acid formed $[Tc_2Cl_8O_2]^{2-}$, which decomposed with rupture of the Tc-Tc bond forming $[Tc(OH)OCl_4]^{2-}$ and $[TcCl_6]^{2-}$. The rate of oxidation was first-order in dioxygen concentration but independent of the concentration of the technetium dimer [19]. The thermal stability of $K_3[Tc_2Cl_8]$ was studied, and it was shown that the anion was stable to 374 °C, whereupon thermal decomposition commenced and was accompanied by disproportionation at 426 °C. One of the disproportionation products was identified as the technetium(IV) species $K_2[TcCl_6]$, which remained unchanged thereafter [23].

In tripolyphosphate solution, the products of the electroreduction of $[TcO_4]^-$ were shown to be pH dependent, with technetium(III) and technetium(IV) formed above pH 7. The solution and electrochemistry of the Tc(III)/Tc(IV) couple have been studied [9].

Complexes of ${}^{99}Tc$ in oxidation states (III) and (IV) with aminopolycarboxylate anions, including edta, dtpa, hedta, nta and ehida (*N*-{2,6-diethylphenylcarbamoylmethyl}iminodiacetate), were investigated by various techniques, and preparative methods and results were reported [24]. The formation of ^{99}Tc complexes of edta, dtpa, ada and hida was studied by various electrochemical techniques, and the nature of the products related to reaction conditions [8].

3.5 TECHNETIUM(III)

Cationic lipophilic complexes such as *trans*-[^{99m}Tc(diars)$_2$Br$_2$]Br (*1*) and *trans*-[^{99m}Tc(dmpe)$_2$Cl$_2$]Cl (*2*) were prepared and used for imaging hepatobiliary and myocardial systems. Complex (*1*) was prepared in 65% yield by heating a mixture of alcoholic hydrobromic acid, Na[^{99m}TcO$_4$] and diars. Complex (*2*) was prepared similarly using alcoholic hydrochloric acid and dmpe [25].

Nine pairs of technetium(III)/technetium(II) complexes of the formula *trans*-[TcL$_2$X$_2$]$^{+/0}$, (L = dmpe, dppb, dppee, dppe or depe; X = Br, Cl or SCN) have been prepared and characterised. The most practical route was by reduction of a higher oxidation state of technetium using an excess of phosphine. The complex *trans*-[Tc(dppe)$_2$Br$_2$][BF$_4$] was characterised by single crystal X-ray diffraction, and the cation is shown in Fig.3:

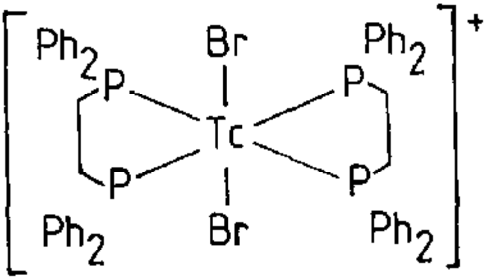

Fig.3: *trans*-[Tc(dppe)$_2$Br$_2$]$^+$

The technetium(III) centre has approximately octahedral symmetry, with four equatorial phosphorus atoms and two axial bromine atoms. Other complexes in the series have been characterised by elemental analysis, IR and electronic spectroscopy, chromatography, magnetic measurements and cyclic voltammetry. All complexes exhibited a characteristic charge-transfer band in the visible spectrum. In dmf solution, every complex showed a reversible Tc(III)/Tc(II) redox couple, with the potential being a function of the coordinating ligands. A Tc(II)/Tc(I) cathodic wave was observed but there was no evidence for a Tc(IV)/Tc(III) couple [26].

The complexes [TcL$_3$] (HL = 1,1-diethyl-, piperidino- or morpholino-3-benzoylthiourea) were prepared by the reduction of [^{99}TcO$_4$]$^{2-}$ with tin(II) chloride in the presence of an excess of the ligand HL. The complexes were all air-stable, and the ligand was bidentate through *S* and *O*. Characterisation was by IR spectroscopy [14].

Oxotetrakis(tetramethylthiourea)technetium(V) hexafluorophosphate, whose preparation was also described, was used to prepare, among other complexes, hexakis(dimethylthiourea)technetium(III) hexafluorophosphate. Spectral, conductivity and magnetic data were reported [18].

In tributylphosphate solution, electroreduction of a technetate(VII) solution yields predominantly technetium(III) below pH 7, while a mixture of technetium(III) and technetium(IV) is formed above pH 7. The solution and electrochemistry of the technetium(III)/technetium(IV) couple were studied [9].

Complexes of ^{99}Tc(III) with aminopolycarboxylate anions, including edta, dtpa, hedta, nta, ada, ehida and hida, were investigated by various techniques, including electrochemical methods, and the preparations and results were discussed [6,24].

3.6 TECHNETIUM(II)

A review has been published with 31 references on the preparation of [^{99}TcL$_2$X$_2$] complexes, where L is a ditertiary phosphine or arsine ligand and X is a halide. Their X-ray structural analysis, electrochemical behaviour and potential as myocardial imaging agents were discussed [27].

Nine pairs of Tc(III)/Tc(II) complexes of the formula *trans*-[TcL$_2$X$_2$]$^{+/0}$ (where L is a chelating ditertiary phosphine, and X is Cl, Br or SCN) have been prepared and characterised. The most practical route is by reduction of a higher oxidation state of technetium with an excess of phosphine. Characterisation was by standard analytical and spectral techniques. All complexes exhibited a characteristic charge-transfer band in the visible spectrum and, in dmf solution, a reversible Tc(III)/Tc(II) redox couple. A Tc(II)/Tc(I) cathodic wave has been observed, but there was no evidence for a Tc(IV)/Tc(III) couple [26].

The technetium(II) complexes $M_2[Tc_2Cl_6].2H_2O$, $M_2[Tc_2Br_6].2H_2O$, (M = K or [NH$_4$]), $\{TcBr_2.0.5H_2O\}_n$ and $\{TcI_2.0.5H_2O\}_n$ and the mixed-valence complex $Tc_2(O_2CMe)_4Br$ have been prepared by the disproportionation of higher oxidation states of technetium in the presence of the hydrogen halide or, in the latter case, hydrochloric acid and ethanoic acid. Reactions were carried out in an autoclave, and products characterised by elemental analysis and various spectral techniques [28].

3.7 TECHNETIUM(I)

The complexes $[Tc(CNR)_6][PF_6]$ (R = CMe_3, Me, cych or Ph) have been prepared by the reduction of the technetate(VII) ion with aqueous sodium dithionite solution in the presence of the isocyanide ligands. These complexes have been characterised by analytical, spectral and electrochemical methods [29].

Hydridobis{1,2-bis(diphenylphosphino)ethane}dinitrogentechnetium(I) crystals were studied by single-crystal X-ray diffraction, and the structure, shown in Fig.4, was described. The technetium is octahedrally coordinated with the hydrido ligand *trans* to the dinitrogen ligand. NMR spectra are presented [30].

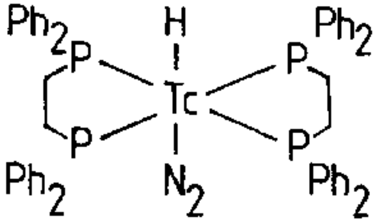

Fig.4: $[TcH(dppe)_2(N_2)]$

3.8 MIXED OXIDATION STATES

The complex $Tc_2(O_2CMe)_4Br$ was prepared by the disproportionation of higher oxidation states of technetium in the presence of hydrobromic acid and ethanoic acid. The reaction was carried out in an autoclave, and the product characterised by various spectral and analytical techniques [28]. The crystal structure of this complex, presented in Fig.5, was determined and showed the molecule to consist of $[Tc_2(O_2CMe)_4]^+$ cations bridged by bromide ions to form linear chains. The Tc-Tc bond order was between three and four [31].

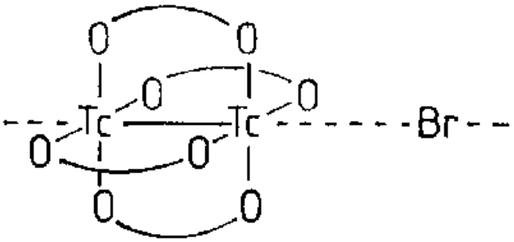

Fig.5: $Tc_2(O_2CMe)_4Br$

The EPR spectra and magnetic susceptibility of the complexes $Tc_2(O_2CR)_4X$ (R = Me, X = Cl or Br; R = CD_3, X = Cl),$K[Tc_2(O_2CMe)_4Cl_2]$ and $[NH_4]_3[Tc_2Cl_8].2H_2O$ were recorded, and studies indicated that the paramagnetism was due to one unpaired electron on two technetium atoms. A detailed analysis was presented [32].

The behaviour of $[Tc_2Cl_8]^{3-}$ in hydrochloric acid solution was studied and shown to depend on the concentrations of the species present, the temperature and the presence of other complexing agents and aerial dioxygen in the solution. Acid hydrolysis through the species $[Tc_2Cl_{8-x}(H_2O)_x]^{(3-x)-}$ eventually yielded $Tc_4O_5.nH_2O$. Complexation of $[Tc_2Cl_8]^{3-}$ with chloride ion led to the unstable $[Tc_2Cl_9]^{4-}$ which rapidly decomposed to mononuclear disproportionation products. In the presence of dioxygen in hydrochloric acid solution, $[Tc_2Cl_8]^{3-}$ initially formed $[Tc_2Cl_8O_2]^{3-}$ which decomposed to

$[Tc(OH)OCl_4]^{2-}$ and $[TcCl_6]^{2-}$. The reaction with other hydrogen halides was also investigated, leading to substituted derivatives of the chloro species [19]. The reactions of $[Tc_2Cl_8]^{3-}$ in HCl were monitored spectrophotometrically, and a mechanism proposed to explain the metal-metal bond cleavage [33]. The thermal stability and decomposition of the potassium salt $K_3[Tc_2Cl_8]$ were studied by DTA, IR spectroscopy and X-ray diffraction. The anion was observed to be stable to 374 °C, whereon thermal decomposition took place in stages, accompanied by disproportionation at 426 °C. One of the disproportionation products was identified as potassium hexachlorotechnetate(IV). Ultimately, technetium metal was deposited as the other disproportionation product [23].

The molecular structure of $[Tc_8Br_{12}][(H_2O)_2H]Br$ was determined. The crystal consisted of $[Tc_8Br_{12}]$, Br^- and $[(H_2O)_2H]^+$, the technetium species being a very complex moiety, with four quadruple Tc-Tc bonds, eight bridging bromines and four terminal bromines [34].

3.9 BINARY COMPOUNDS

Reaction of technetium with red phosphorus, using the tin flux method or iodine as mineralizer, yielded six technetium phosphides: Tc_3P crystallised in the tetragonal Fe_3P structure, isotypic with Mn_3P, while TcP_4 had the orthorhombic ReP_4 structure. These two compounds were studied by X-ray diffraction and the refined structures presented. The other four phosphides were reported to have the approximate compostions $TcP_{0.7}$, $TcP_{1.3}$, TcP_2 and TcP_3. The structures and compositions were discussed at length [35]. The compound TcP_3 was also examined by single crystal X-ray diffraction, and the structure presented. The metal atoms were six-coordinate, while the phosphorus atoms were tetrahedrally coordinated to phosphorus and technetium, with formal oxidation numbers 0, -1 and -2. The metal was consequently deduced to have a formal oxidation state of +3 [36].

The electronic structure and partial densities of states of TiTc were calculated by the non-relativistic APW method within a muffin-tin approximation [37].

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