

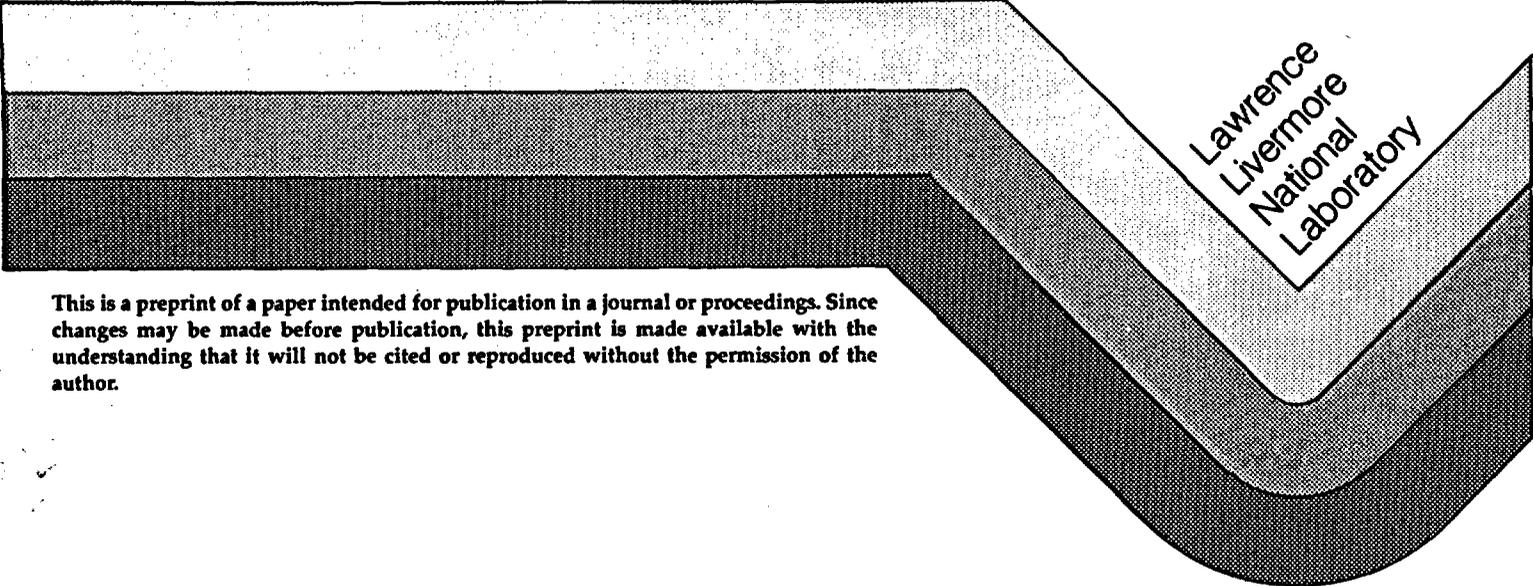
CHEMICAL THERMODYNAMICS OF TECHNETIUM

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This manuscript by J.A. Rard is to be part of a book entitled "CHEMICAL THERMODYNAMICS OF TECHNETIUM". It will be published by the Nuclear Energy Agency Data Bank at Saclay, France. There will also be technical contributions from Malcolm Rand (Harwell, U.K.), John Thornback (Loughborough, U.K.; presently at Harvard Medical School), and P.P.S. Saluja (Whiteshell, Canada). These contributions will be combined and edited at NEA by Hans Wanner; he will also put the contributions on a consistent basis. The authorship will be J.A. Rard, M.H. Rand, P.P.S. Saluja, and J. Thornback.

This book will contain an introduction and a discussion of standards and conventions (Sections I and II). They have been written at NEA and are common to their reviews for all elements of interest. Section III will give the selected thermodynamic data, and will be compiled and written by Hans Wanner from the contributions of the various authors.

Section IV, discussion of data selection, will contain my contribution and that of the other authors. Their contributions are to cover:

1) **Malcolm Rand**

- 1. Elemental technetium
- 3.1.1 Halogen compounds (monomeric technetium halides)
- 6.1.1 Inorganic carbon compounds
- 6.3.1 Silicon compounds
- 8. Boron compounds
- 10. Intermetallic compounds

2) **P.P.S. Saluja**

- 2.1 Oxide compounds
- 2.3 Hydroxide compounds
- 2.4 Oxo and hydroxo complexes
- 3.2 Halogen complexes
- 5.2.2 Phosphorus complexes
- 6.1.1 Inorganic carbon complexes
- 6.3.2 Silicon complexes
- 9. Pertechnetate salts

3) **John Thornback**

7.1 **Organic compounds**

7.2 **Organic complexes**

CHEMICAL THERMODYNAMICS OF TECHNETIUM

Contributions to the NEA Book on Technetium Thermodynamics: Hydrides, Polynuclear Halides, Oxohalides, Hydroxohalide Salts, Oxohalide Salts, Chalcogenides and Chalcogen Complexes, Oxosulphur Complexes, Nitrogen Compounds, Nitrogen Complexes, Phosphorus Compounds, Other Pnictide Compounds and Complexes (As, Sb, Bi), Pseudo-halide and Oxopseudo-halide Complexes, Nitrosyl Complexes, and Tin Complexes

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IV. Discussion of Data Selection

2. Oxide, Hydride, and Hydroxide Compounds and Complexes

2.2 Hydride Compounds

Metallic technetium shows little tendency to react with hydrogen under conditions of ambient temperature and pressure. However, in 1979, Spitsyn and co-workers (SP79) reported synthesizing solid $TcH_{0.73 \pm 0.05}$ by using hydrogen pressures of up to 19 kbar at 573 K. This $TcH_{0.73 \pm 0.05}$ formed as a single phase with a hexagonal lattice with $a = (2.805 \pm 0.01) \times 10^{-10}$ m and $c = (4.455 \pm 0.01) \times 10^{-10}$ m; both c and a are expanded by about 0.06×10^{-10} m from the pure metal values. At room temperature and one atmosphere pressure it took several months for this hydride to spontaneously decompose, and it was chemically stable during isothermal annealings up to about 470 K. However, with continuous heating under open conditions it decomposed back to the metal and hydrogen above 350 K.

Spitsyn and co-workers (SA81) varied hydrogen pressures from low pressures to about 22 kbar at 573 K and studied the Tc-H₂ isotherm. Below about 1 kbar Sievert's law was observed for dissolution of hydrogen; that is, TcH_m formed with $m \propto (P_{H_2})^{1/2}$. As the H₂ pressure was increased, the

solubility of H_2 increased rapidly up to about 5 kbar applied H_2 pressure, it was then nearly constant to about 9 kbar, it rose steeply to about 15 kbar, and then had another plateau. The first plateau corresponded to formation of $TcH_{0.5}$, and the second to $TcH_{0.78}$. The initial addition of hydrogen reduced the superconducting transition temperature of Tc about 0.5 K to 7.35 K, whereupon it remained constant for $0.04 \leq m \leq 0.26$. For $m > 0.39$ no superconductivity was observed above 2 K, which was the lowest temperature studied.

Samples of $TcH_{0.45}$ and $TcH_{0.69}$ were later studied by neutron diffraction (GI84,SG85). Both hydrides were indexed for hexagonal cells with $a=(2.801\pm 0.002) \times 10^{-10}$ and $c=(4.454\pm 0.005) \times 10^{-10}$ m for $TcH_{0.45}$, and $a=(2.838\pm 0.002) \times 10^{-10}$ and $c=(4.645 \pm 0.005) \times 10^{-10}$ m for $TcH_{0.69}$. Three unexpected diffraction peaks were observed for $TcH_{0.45}$, which they interpreted as evidence for a superstructure. They concluded that hydrogen occupied octahedral interstices in the technetium lattice.

There are no experimental thermodynamic data for solid TcH_m . However, Bouten and Miedema (BM80) estimated that $\Delta_f H_m^\circ = +9 \text{ kJ}\cdot\text{g}\cdot\text{atom}^{-1}$ for $Tc_{0.5}H_{0.5}$. This positive value indicates that it should spontaneously decompose, as is observed to happen.

Floss and Grosse (FG60) reduced TcO_4^- with a NH_4ReO_4 carrier using potassium in ethylenediamine to yield the ternary hydride $K[ReH_4]\cdot nH_2O$ where $n=2-4$. The technetium cocrystallized in the rhenium hydride, presumably as $K[(Re,Tc)H_4]\cdot 2H_2O$. This material could be dissolved in cold aqueous KOH with slow decomposition, but when it was added to dilute HCl the decomposition was rapid.

Ginsburg (G64) repeated this preparation in an ethylenediamine-ethanol mixture using carrier free NH_4TcO_4 . The resulting crystals were hexagonal with $a = 9.64 \times 10^{-10}$ and $c = 5.56 \times 10^{-10}$ m, and they were shown to be isostructural with K_2ReH_9 . Thus, the technetium compound is K_2TcH_9 . Small quantities of K_2TcH_9 could be dissolved in 20-50 % aqueous KOH without excessive decomposition, but decomposition was rapid when > 0.05 % K_2TcH_9 was added. Alkaline solutions of TcH_9^{2-} reduced Tl^+ to metallic thallium, and NaOCl converted TcH_9^{2-} to TcO_4^- . A NMR study of TcH_9^{2-} in aqueous 40 % KOH indicated a non-rigid

(fluxional) anion (FL82). A molecular orbital description is available for TcH_9^{2-} (BG69). No thermodynamic data are available, but K_2TcH_9 decomposes under normal environmental conditions.

Mastryukov (M72) estimated that the bond dissociation energy for TcH(g) is 198-243 $\text{kJ}\cdot\text{mol}^{-1}$ based on correlations for hydrides of other elements. A value of 174 $\text{kJ}\cdot\text{mol}^{-1}$ was estimated by Langhoff et al. (LP87) from quantum mechanical calculations using the coupled pair functional method with relativistic effective core potentials, and 195 $\text{kJ}\cdot\text{mol}^{-1}$ by using a modification of this method. No experimental value is available for comparison.

3. Halogen Compounds and Complexes

3.1 Halogen Compounds

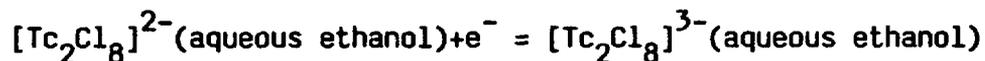
3.1.2 Binuclear Halides

In 1963 Eakins et al. (EH63a) described the preparation of solid $[\text{Tc}_2\text{Cl}_8]^{3-}$ compounds and their solutions. They were produced by reduction of aqueous TcCl_6^{2-} salts at 373 K by using zinc metal in oxygen-free concentrated HCl. They thus prepared $(\text{NH}_4)_3[\text{Tc}_2\text{Cl}_8]\cdot 2\text{H}_2\text{O}$, $\text{Y}[\text{Tc}_2\text{Cl}_8]\cdot 9\text{H}_2\text{O}$, and $\text{K}_3[\text{Tc}_2\text{Cl}_8]\cdot n\text{H}_2\text{O}$, all of which should contain mixed valence Tc(II,III). Oxidation studies confirmed that the average technetium valence in these compounds was Tc(2.5). Spitsyn et al. prepared the corresponding pyridinium $(\text{PyH})_3[\text{Tc}_2\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ and quinolinium $(\text{QuinH})_3[\text{Tc}_2\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ salts by using reduction of HCl solutions of the corresponding TcCl_6^{2-} salt in an autoclave with H_2 at 30.4 bar pressure (SK77a, SK77b). In one of these studies (SK77a), both the HCl concentration and reaction temperature were varied; although the color of the solution during reaction changed both with HCl concentration and with temperature, the final product was the same in each case.

Some reports of the reduction of pertechnetate salts by H_2 in an autoclave contain the claim that the products were actually $\text{K}_8[\text{Tc}_2\text{Cl}_8]_3\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_8[\text{Tc}_2\text{Cl}_8]_3\cdot 2\text{H}_2\text{O}$, and $\text{Cs}_8[\text{Tc}_2\text{Cl}_8]_3\cdot 2\text{H}_2\text{O}$ (GK73, KN75). Although it is possible that hydrogen reduction could give a less reduced product with a lower monovalent cation-to-technetium ratio than reduction by zinc metal, it seems unlikely since unit cell parameters reported for $\text{K}_3[\text{Tc}_2\text{Cl}_8]\cdot n\text{H}_2\text{O}$ and $\text{K}_8[\text{Tc}_2\text{Cl}_8]_3\cdot 4\text{H}_2\text{O}$ are identical within experimental error, and the

space groups are the same, for both crystals (CS75, KN75). It is thus reasonable to assume identical compounds were prepared in both studies, and the simpler formulation $M_3[Tc_2Cl_8] \cdot nH_2O$ will be accepted.

In 1975 Cotton and Pedersen (CP75) found that the reaction



occurred quasireversibly at 0.38 V in a mixture of 10 % 12 mol·dm⁻³ aqueous HCl and 90 % ethanol. Since the lifetime of $[Tc_2Cl_8]^{2-}$ was found to be $\gg 300$ s, it was clear that it could be possible to prepare solid compounds containing this anion.

In 1977 Schwochau et al. (SH77) reported preparation of such a salt, $[n-(C_4H_9)_4N]_2[Tc_2Cl_8]$, using reduction of TcO_4^- by H_3PO_2 in aqueous HCl. However, Cotton et al. (CD81) reported that attempts to prepare that compound with reduction by H_3PO_2 gave $[TcOCl_4]^-$ salts instead.

Pretz and Peters (PP80a) reduced $[TcCl_6]^{2-}$ by using zinc in concentrated HCl, evaporated the solution and then extracted $ZnCl_2$ with diethylether, and obtained a red-brown residue. This residue was dissolved in HCl with $[(n-C_4H_9)_4N]Cl$ added, and the resulting mixture of $[(n-C_4H_9)_4N]_2[Tc_2Cl_8]$ and $[(n-C_4H_9)_4N]_3[Tc_2Cl_8]$ was extracted with CH_2Cl_2 . These two compounds were separated by taking advantage of the greater solubility of green $[(n-C_4H_9)_4N]_2[Tc_2Cl_8]$ in acetone, relative to the grey-blue $[(n-C_4H_9)_4N]_3[Tc_2Cl_8]$. This method of preparing $[Tc_2Cl_8]^{2-}$ was confirmed by Cotton et al. (CD81), who characterized the structure of this salt. Since both Cotton et al. (CD81) and Schwochau et al. (SH77) reported the same structure type and very similar unit cell dimensions, their products must be identical. However, the details of preparation of $[(n-C_4H_9)_4N]_2[Tc_2Cl_8]$ by reduction of $TcCl_6^{2-}$ with H_3PO_2 need to be more clearly defined. Pretz and Peters (PP80a) also prepared carmine red $[(n-C_4H_9)_4N]_2[Tc_2Br_8]$, by reacting $[(n-C_4H_9)_4N]_2[Tc_2Cl_8]$ with bromine-free concentrated HBr in acetone.

A third type of binuclear complex has also been reported by Kryuchkov et al. (KK82, GK86): $M_2[Tc_2Cl_6] \cdot nH_2O$ where $M^+ = NH_4^+$ or alkali metal cation. These are prepared from $MTcO_4$ salts in hydrochloric acid by use

of reduction with H_2 at 30.4 bar in an autoclave at 413-423 K. One of these compounds, $K_2[Tc_2Cl_6] \cdot 2H_2O$, was described in detail and structurally characterized (KG86a). It formed star-shaped concretions together with $K_3[Tc_2Cl_8] \cdot nH_2O$ in the reaction vessel. If the reaction was done with tetraalkylammonium salts present instead of ammonium or alkali metal, then polynuclear clusters were obtained (GK86). These are described in the next section.

Crystal structure data have been reported for a number of these binuclear technetium chlorides (KN75, CS75, SH77, CD81, KG86a, CB65, BC70, KN72, CD82), and the structural information are summarized in Table 1. For $[Tc_2Cl_8]^{3-}$, the symmetry is approximately D_{4h} , with an eclipsed $Cl_4Tc-TcCl_4$ structure and a Tc-Tc bond length of about $(2.11-2.14) \times 10^{-10}$ m. For $[Tc_2Cl_8]^{2-}$, the Tc-Tc bond length is about 2.15×10^{-10} m (CD81). The positions of $[Tc_2Cl_8]^{2-}$ in the $[(n-C_4H_9)_4N]^+$ salt are disordered. In $K_2[Tc_2Cl_6]$, the $Tc_2Cl_8^{4-}$ fragments are linked by bridging chlorine atoms into infinite $[Tc_2Cl_6]_n^{2n-}$ zigzag chains (KG86a).

Magnetic susceptibilities have been reported for $K_3[Tc_2Cl_8] \cdot nH_2O$ (ZS73), $Cs_3[Tc_2Cl_8] \cdot 2H_2O$ (ZS73), $(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$ (BC70, CP75), $Y[Tc_2Cl_8] \cdot 9H_2O$ (CP75), $(QuinH)_3[Tc_2Cl_8] \cdot 2H_2O$ (SK77b), and the alleged compounds $K_8[Tc_2Cl_8]_3 \cdot 4H_2O$ and $Cs_8[Tc_2Cl_8]_3 \cdot 2H_2O$ (GK73). In each case the magnetic susceptibilities yielded magnetic moments of about 2 BM,* which indicated the presence of one unpaired electron.

The thermal stability of $K_3[Tc_2Cl_8] \cdot 2H_2O$ in argon has been studied by differential thermal analysis, IR spectroscopy, and x-ray diffraction (OK82). This compound underwent dehydration to $K_3[Tc_2Cl_8]$ at 433 K, followed by disproportionation to $K_2[Tc_2Cl_6]$, KCl, and Tc metal at 699 K. Crystallization of Tc metal began around 873 K.

A similar thermal decomposition study was done for $(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$ in argon and argon-helium mixtures (SK87). Water was lost between 413 and 443 K; anhydrous $(NH_4)_3[Tc_2Cl_8]$ decomposed to technetium metal, $(NH_4)_2TcCl_6$, NH_4Cl , and Cl_2 around 553-613 K; and the $(NH_4)_2TcCl_6$ then decomposed to TcN via a claimed TcNCl intermediate.

*The non-S.I. unit Bohr Magneton = $9.274 \times 10^{-24} J \cdot T^{-1}$.

Solutions of $[\text{Tc}_2\text{Cl}_8]^{3-}$ are relatively "stable" under mildly reducing conditions in HCl, but they decompose in the presence of oxygen. Extraction of $[\text{Tc}_2\text{Cl}_8]^{3-}$ with CH_2Cl_2 from its HCl solution in the presence of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Cl}$ in air converts it to the compound $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Tc}_2\text{Cl}_8]$ (CD81). Aqueous HCl solutions of $[\text{Tc}_2\text{Cl}_8]^{3-}$ gradually are oxidized further to yellow TcCl_6^{2-} by oxygen in air (BC70). However, even in the absence of oxygen, solutions of $[\text{Tc}_2\text{Cl}_8]^{3-}$ slowly decompose to TcCl_6^{2-} over a several day period (SK77b).

Spitsyn et al. (SK77a) noted that reduction of $(\text{PyH})_2[\text{TcCl}_6]$ by molecular hydrogen in an autoclave produced different colored solutions during reduction, depending on the HCl concentration used, but the final reduction product was always $(\text{PyH})_3[\text{Tc}_2\text{Cl}_8] \cdot 2\text{H}_2\text{O}$. The colors were blue in $7 \text{ mol} \cdot \text{dm}^{-3}$ HCl, green in $5\text{-}6 \text{ mol} \cdot \text{dm}^{-3}$ HCl, and brown in $4\text{-}4.5 \text{ mol} \cdot \text{dm}^{-3}$ HCl. They accounted for these color differences in terms of the formation of an intermediate species $[\text{TcCl}_4(\text{OH})_2]^{2-}$ at lower HCl concentrations. The reverse process, decomposition of $[\text{Tc}_2\text{Cl}_8]^{3-}$ with changing HCl concentrations, has been studied in more detail both in the absence and presence of oxygen (SK80, K81, KK83).

Spitsyn et al. (SK80) studied aquation of $[\text{Tc}_2\text{Cl}_8]^{3-}$ in O_2 -free HCl at different HCl concentrations. The solution color varied from azure blue in $5.0\text{-}9.0 \text{ mol} \cdot \text{dm}^{-3}$ HCl at 293 K, to dark brown in the absence of HCl at $\text{pH} \sim 10$. Electrophoresis measurements indicated that the effective charge on the cluster varied from -3.0 ± 0.4 in $5.0\text{-}9.0 \text{ mol} \cdot \text{dm}^{-3}$ HCl to $+3.4 \pm 0.7$ at $\text{pH} = 10$, which indicates stepwise aquation is occurring with increasing pH. The optical absorbance of these solutions was monitored as a function of pH and time. They saw little evidence for oxidation of the dimer in the absence of O_2 , and proposed that the black solid that precipitates was $\text{Tc}_4\text{O}_5 \cdot n\text{H}_2\text{O}$. Magnetic susceptibilities gave an effective magnetic moment of 2.5 BM, which indicates the presence of a single unpaired electron. If, however, HCl can oxidize the hydrolyzed species, then the average valence of technetium in this hydrous oxide could be higher. Their proposed stepwise aquation of $[\text{Tc}_2\text{Cl}_8]^{3-}$ involves $[\text{Tc}_2\text{Cl}_{8-n}(\text{H}_2\text{O})_n]^{-3+n}$ intermediates (K81).

In the presence of O_2 , the decomposition of $[Tc_2Cl_8]^{3-}$ involves a more complex mechanism (K81, KK83). They suggested that competing processes occur: acid induced aquation, disproportionation of the dimer with rupture of the Tc-Tc bond, and also oxidative addition of O_2 to the dimer with subsequent rupture of the Tc-Tc bond. It has been claimed that Tc(II) species and $[TcCl_6]^{2-}$ form by disproportionation of $[Tc_2Cl_8]^{3-}$ for HCl concentrations $>3 \text{ mol}\cdot\text{dm}^{-3}$ in the absence of O_2 (KK83), and that $[TcCl_6]^{2-}$ and $[TcOCl_4(OH)]^{2-}$ form in the presence of O_2 (K81). As the concentration of HCl is reduced, $[TcCl_6]^{2-}$ can undergo hydrolysis, and, at high enough pH values, hydrated TcO_2 should precipitate. Aqueous solutions of $[Tc_2Cl_8]^{3-}$ reacts with O_2 -free HF and HI to form $[Tc_2F_8]^{3-}$ and $[Tc_2I_8]^{3-}$, respectively (K83).

Decomposition of $[Tc_2Br_8]^{3-}$ by O_2 from air has only been studied in $8 \text{ mol}\cdot\text{dm}^{-3}$ HBr at 298 K (KS87). The oxidation was first order in $[Tc_2Br_8]^{3-}$ with an effective rate constant of $(2.5 \pm 1.2) \times 10^{-4} \text{ s}^{-1}$. Extinction coefficients for both $[Tc_2Br_8]^{3-}$ and $[TcBr_6]^{2-}$ were measured spectrophotometrically.

Although none of these binuclear technetium halides have thermodynamic data, they are unstable under typical environmental conditions since they hydrolyze and are readily oxidized by O_2 .

3.1.3 Polynuclear Technetium Halides

Rinke et al. (RK67) prepared a mixed rhenium-technetium trichloride by reducing an aqueous NH_4ReO_4 - NH_4TcO_4 solution to technetium metal with hydrogen, followed by chlorination. The final material had a Re to Tc atomic ratio of 2.7:1. Mass spectra measurements at 873-723 K indicated the presence of a number of gas phase ions. "Parent" gas phase molecules for technetium species were apparently $TcCl_4$, Tc_3Cl_9 , Tc_2ReCl_9 , $TcRe_2Cl_9$, Tc_3Cl_{12} , and Tc_2ReCl_{12} . The presence of trinuclear technetium chlorides in the gas phase suggests that it might also be possible to prepare polynuclear halides in the solid state.

The first reports of solid polynuclear technetium halide compounds (three or more technetium atoms) appeared in 1982. Kryuchkov et al. (KK82) found

that both HTcO_4 and H_2TcBr_6 in concentrated HBr were reduced by H_2 at 30.4 bar and 413-423 K in an autoclave to produce black crystals of material with the empirical composition " $(\text{TcBr}_2 \cdot 0.5\text{H}_2\text{O})_n$ ". This material was dissolved by aqueous acids, and it was slowly hydrolyzed by water and bases. Similarly, reduction of HTcO_4 , H_2TcI_6 , KTcO_4 , and NH_4TcO_4 in concentrated HI at the same temperature and H_2 pressure yielded black crystals of material with the empirical composition " $(\text{TcI}_2 \cdot 0.5\text{H}_2\text{O})_n$ ". It was only slightly soluble in HI , and it was hydrolyzed by water and bases. Both "compounds" were diamagnetic, and neither of them reacted with acetic acid under autoclave conditions. This latter property suggests they are polymeric. Binding energies of Tc 3d 5/2 electrons for these compounds as determined by x-ray electron spectroscopy are in the range found for Tc(II) compounds (GK82).

Kryuchkov et al. (KK82) also noted that their method of synthesis actually gave mixtures of crystals of various compounds, so " $(\text{TcX}_2 \cdot 0.5\text{H}_2\text{O})_n$ " is an approximate overall formula. Both bromide and iodide ions gave mixtures of various polymeric clusters that can be represented by the more general formula $(\text{TcX}_{1.8 \pm 0.3})_m \cdot n\text{H}_2\text{O}$. Crystals of one of these compounds " $\text{Tc}_8\text{Br}_{13} \cdot 2\text{H}_2\text{O}$ " were separated from the mixture, and a single crystal structural analysis performed (KS82). The crystals are monoclinic, and they are of space group $\text{P2}_1/\text{n}$ with $a = (7.561 \pm 0.002) \times 10^{-10}$, $b = (13.553 \pm 0.005) \times 10^{-10}$, $c = (12.620 \pm 0.003) \times 10^{-10}$ m, $\beta = 102.62 \pm 0.02^\circ$, and $Z = 2$. This compound contains the octameric cluster $\text{Tc}_8\text{Br}_{12}$, and Br^- ions. Within the analytical uncertainty of the composition of this compound, the " H_2O " molecules could actually be $[(\text{H}_2\text{O})_n\text{H}]^+$ or OH^- . Thus the charge on the cluster is uncertain. Their proposed structure has half of the technetiums bonded to four others, and the other technetiums bonded to three others.

In 1983 Koz'min et al. (KL83) reported preparation of two additional reduced valence technetium halide cluster compounds using the same basic method of autoclave synthesis under hydrogen pressure. They prepared orthorhombic crystals of $[(\text{CH}_3)_4\text{N}]_3[\text{Tc}_6\text{Cl}_{14}]$, that are of space group Pcmn with $a = (11.583 \pm 0.002) \times 10^{-10}$, $b = (13.527 \pm 0.003) \times 10^{-10}$, $c = (24.387 \pm 0.003) \times 10^{-10}$ m, and $Z=4$. The uncertainty for 'b' contains a misprint in the English translation. The $[\text{Tc}_6\text{Cl}_{14}]^{3-}$ clusters have

technetium atoms in a trigonal prism arrangement whose base is in the form of a right triangle, with three bridging chlorine atoms on each end bonded to pairs of technetium atoms. Thus the structure should be written as $[(\text{CH}_3)_4\text{N}]_3[\text{Tc}_6\text{Cl}_6\mu\text{-Cl}_6]\text{Cl}_2$ (SK85).

They (KL83) also reported preparation of $[(\text{H}_2\text{O})_3\text{H}_3\text{O}]_2[\text{Tc}_6(\text{Br},\text{OH})_6\text{Br}_6]$ which forms monoclinic crystals of space group $\text{P}2_1/c$ with $a = (9.258 \pm 0.004) \times 10^{-10}$, $b = (9.211 \pm 0.003) \times 10^{-10}$, $c = (17.437 \pm 0.007) \times 10^{-10}$ m, $\beta = 101.09 \pm 0.03^\circ$, and $Z = 2$ (KL83). The $[(\text{H}_2\text{O})_3\text{H}_3\text{O}]^+$ cations consist of a H_3O^+ whose oxygen atom is bonded to three water oxygens by hydrogen bonds. The $[\text{Tc}_6(\text{Br},\text{OH})_6\text{Br}_6]^{2-}$ anion has six technetium atoms in an octahedral arrangement inscribed in a cube, with six apices occupied by bromine atoms and, possibly, some hydroxyl oxygens, with two sites unoccupied. Some of the bromine atom positions are disordered.

German et al. (GK86) noted that reduction of TcO_4^- or TcCl_6^{2-} salts in concentrated HCl with alkali metal chloride or ammonium chloride present gave preferential formation of $\text{M}_2[\text{Tc}_2\text{Cl}_6] \cdot n\text{H}_2\text{O}$, but in the presence of n-tetraalkylammonium salts a number of polynuclear cluster compounds were produced instead. Using autoclave synthesis with $[(\text{CH}_3)_4\text{N}]_2\text{TcCl}_6$ and 50.7 bar hydrogen pressure at 433-453 K, they produced black crystals of $[(\text{CH}_3)_4\text{N}]_2[\text{Tc}_6\text{Cl}_6\mu\text{-Cl}_6]$, which crystallizes in the space group P1 with $a = (11.614 \pm 0.004) \times 10^{-10}$, $b = (11.633 \pm 0.004) \times 10^{-10}$, $c = (14.017 \pm 0.006) \times 10^{-10}$ m, $\alpha = 69.66^\circ$, $\beta = 65.89^\circ$, $\gamma = 60.13^\circ$, and $Z=2$. In this cluster, the technetium atoms occur in a prism with three chloride atoms on each end shared between two technetiums each. Like $[(\text{CH}_3)_4\text{N}]_3[\text{TcCl}_6\mu\text{-Cl}_6]\text{Cl}_2$, $[(\text{CH}_3)_4\text{N}]_2[\text{Tc}_6\text{Cl}_6\mu\text{-Cl}_6]$ forms a brown solution when it is dissolved in warm concentrated HCl.

Koz'min et al. (KS85a) elsewhere gave more details of the structures of $[(\text{CH}_3)_4\text{N}]_3[\text{Tc}_6\text{Cl}_6\mu\text{-Cl}_6]\text{Cl}_2$ and $[(\text{CH}_3)_4\text{N}]_2[\text{Tc}_6\text{Cl}_6\mu\text{-Cl}_6]$ (GK86). They also compared these structures to those of " $\text{Tc}_8\text{Br}_{12}$ " clusters.

Kruchkov et al. (KK86) reinvestigated polynuclear technetium bromides. Their earlier study (KL83) did not allow location of hydrogen atoms in " $[(\text{H}_2\text{O})_3\text{H}_3\text{O}]_2[\text{Tc}_6(\text{Br},\text{OH})_6\text{Br}_6]$ ", so there was some ambiguity as to whether this compound contained OH^- , H_2O , or H_3O^+ groups. At 413-453 K and 30.4 -50.7 bar of H_2 pressure in concentrated HBr, Kruchkov et al. (KK86) were

able to prepare and then isolate crystals of two compounds from reduction of HTcO_4 or H_2TcBr_6 . Increasing the temperature to 453-473 K at 50.7 bar H_2 gave a third compound. Also, two additional but unidentified compounds were also produced.

Their (KK86) first two compounds were metallic-blue $[\text{H}(\text{H}_2\text{O})_2][\text{Tc}_8\text{Br}_4\mu\text{-Br}_8]\text{Br}$ which possesses the space group $\text{P2}_1/\text{n}$ with $a = (7.561 \pm 0.001) \times 10^{-10}$, $b = (13.553 \pm 0.005) \times 10^{-10}$, $c = (12.620 \pm 0.003) \times 10^{-10}$ m, $\beta = 102.62^\circ$, and $Z = 2$; and black $[\text{H}(\text{H}_2\text{O})_2]_2[\text{Tc}_8\text{Br}_4\mu\text{-Br}_8]\text{Br}_2$ which has the space group $\text{P2}_1/\text{a}$ with $a = (22.151 \pm 0.009) \times 10^{-10}$, $b = (9.026 \pm 0.003) \times 10^{-10}$, $c = (9.396 \pm 0.004) \times 10^{-10}$ m, $\beta = 105.95^\circ$, and $Z = 2$. For both cases, the technetium atoms occur on a rectangle with four μ -bromides bonded to two technetiums apiece on each end, four other bromides singly bonded on opposite sides of the rectangle (two on top, two on bottom), and bridging bromides to form infinite chains. Their third compound was black $[\text{H}_3\text{O}(\text{H}_2\text{O})_3]_2[\text{Tc}_6\text{Br}_6\mu\text{-Br}_5]$ which has the space group $\text{P2}_1/\text{c}$ with $a = (9.258 \pm 0.004) \times 10^{-10}$, $b = (9.211 \pm 0.003) \times 10^{-10}$, $c = (17.437 \pm 0.007) \times 10^{-10}$ m, $\beta = 101.09^\circ$, and $Z = 2$. This last compound is simply a reformulation of the compound described earlier as $[(\text{H}_2\text{O})_3\text{H}_3\text{O}]_2[\text{Tc}_6(\text{Br},\text{OH})_6\text{Br}_6]$ (KL83). There is still some uncertainty in the H_3O^+ , OH^- , and H_2O contents of these three compounds.

One of Kryuchkov et al.'s (KK86) "unidentified compounds" was obtained by boiling a solid residue in excess deaerated HBr . An x-ray structural determination by Kryuchkov et al. (KG86b) of this metallic black monoclinic $[\text{Tc}_8\text{Br}_4\mu\text{-Br}_8]\text{Br} \cdot 2\text{H}_2\text{O}$ showed it was of space group $\text{P2}_1/\text{n}$ with $a = (7.573 \pm 0.002) \times 10^{-10}$, $b = (13.428 \pm 0.003) \times 10^{-10}$, $c = (12.661 \pm 0.002) \times 10^{-10}$ m, $\beta = 103.05 \pm 0.02^\circ$, and $Z=2$. Its cluster has a structure nearly identical to that in $[\text{H}(\text{H}_2\text{O})_2][\text{Tc}_8\text{Br}_4\mu\text{-Br}_8]\text{Br}$, which was already described.

Kryuchkov et al. (KG87) have reported the preparation of two additional polymeric technetium bromides. They prepared $[(\text{CH}_4)_3\text{N}]_3[\text{Tc}_6\text{Br}_6\mu\text{-Br}_6]\text{Br}_2$ by reacting $[(\text{CH}_4)_3\text{N}]_3[\text{Tc}_6\text{Cl}_6\mu\text{-Cl}_6]\text{Cl}_2$ with aqueous $[(\text{CH}_3)_4\text{N}]\text{Br}$ and HBr in an autoclave at 453 K and 40.5 bar H_2 pressure. This reaction also produced another, as of now, unidentified compound in about 50 % yield. Their second identified compound is $[(\text{CH}_3\text{CH}_2)_4\text{N}]_2[\text{Tc}_6\text{Br}_6\mu\text{-Br}_6]\text{Br}_2$, and it

was prepared in an autoclave, also by reduction of $[(\text{CH}_3\text{CH}_2)_4\text{N}]_2[\text{TcCl}_6]$ in aqueous HBr with H_2 at 50.7 bar pressure and at 373 K.

$[(\text{CH}_3)_4\text{N}]_3[\text{Tc}_6\text{Br}_6\mu\text{-Br}_6]\text{Br}_2$ crystallizes in the space group $\text{P6}_3/\text{mmc}$ with $a = (13.781 \pm 0.003) \times 10^{-10}$, $c = (12.801 \pm 0.004) \times 10^{-10}$ m, and $Z=3$ (KG87). It is paramagnetic and gives an anisotropic ESR signal.

$[(\text{CH}_3\text{CH}_2)_4\text{N}]_2[\text{Tc}_6\text{Br}_6\mu\text{-Br}_6]\text{Br}_2$ crystallizes in the triclinic space group $\text{P}\bar{1}$ with $a = (12.877 \pm 0.003) \times 10^{-10}$, $b = (13.684 \pm 0.003) \times 10^{-10}$, $c = (14.613 \pm 0.004) \times 10^{-10}$ m, $\alpha = 81.25 \pm 0.02^\circ$, $\beta = 67.45 \pm 0.02^\circ$, $\gamma = 63.91 \pm 0.02^\circ$, and $Z=2$. It has temperature independent paramagnetism and no ESR signal. In both cases the technetium atoms occur in a prismatic shape with three bridging chlorine atoms on each end shared with two technetiums. The cluster is very similar to that found in $[(\text{CH}_3)_4\text{N}]_2[\text{Tc}_6\text{Cl}_6\mu\text{-Cl}_6]$ (GK86).

No thermodynamic data are available for any of these technetium cluster halides. However, their solutions are somewhat "stable" only in concentrated acid under reducing conditions, so they would decompose under normal environmental conditions.

3.3 Oxohalides and Related Salts

3.3.1 Oxohalides

Two reviews are available for technetium halides and oxohalides that cover the pertinent literature up to the early to mid 1960's (C65, CC68a). They contain discussions of methods of preparation, chemical properties, and thermodynamics and phase behavior.

In 1954, Nelson et al. (NB54) reported that reaction of $\text{TcO}_2(\text{s})$ with Cl_2 at one bar and 573 K produced two products. One of these was dark blue and which was distilled by 357 K; the other sublimed readily at 1173 K and was light brown. Both were paramagnetic. A more detailed reinvestigation of this reaction by Colton and Tomkins (CT68) at 573 K confirmed there were two products. One is blue and highly volatile, but it was observed to be thermally unstable and to decompose to TcOCl_3 when the Cl_2 pressure dropped below about 0.26 bar. The second product was brown, and it sublimed unchanged above 773 K. Chemical analysis confirmed the brown solid is TcOCl_3 . It is readily hydrolyzed with disproportionation to form solid hydrated TcO_2 and aqueous TcO_4^- .

An additional study by Guest and Lock (GL72) showed that there are actually three technetium oxochlorides: TcO_3Cl , TcOCl_4 , and TcOCl_3 . In that study, chlorination of technetium metal was carried out at 573-773 K. Less than 10 % TcCl_4 was produced, with the remainder being a green solid. Trap-to-trap distillation in the dark separated this solid into TcOCl_4 and TcO_3Cl . TcOCl_4 is a purple crystalline solid that melts around 308 K. Samples of TcOCl_4 contaminated with TcO_3Cl appear to be blue. TcOCl_4 is very light sensitive and photodecomposes to brown TcOCl_3 . This photosensitivity, rather than simple thermal instability, may partially account for Colton and Tomkins' observations (CT68).

Heating TcCl_4 with O_2 at 723 K for several hours produces TcO_3Cl , which exists as a pale yellow liquid that boils around 298 K. TcO_3Cl is hydrolyzed readily by dilute aqueous NH_3 to form aqueous TcO_4^- ; similarly, TcOCl_4 can be readily hydrolyzed to form solid hydrated TcO_2 and aqueous TcO_4^- in a 1:2 ratio (GL72).

Rudolph and Bächmann (RB80) studied the high temperature chromatography of gaseous Tc species obtained by reacting Tc metal with CCl_4 , and "observed" the formation of TcOCl_3 and TcOCl_4 . Actually, the presence of these compounds was deduced indirectly and not directly determined. Rulfs et al. (RP67) claimed that TcO_3Cl formed when TcO_4^- was added to concentrated H_2SO_4 containing Cl^- . However, Guest and Lock (GL72) noted that their optical spectra for pure TcO_3Cl was inconsistent with that for the solution species of Rulfs et al. (RP67). Also see sect. 3.3.3.

Reaction of Br_2 vapor with solid TcO_2 at 573-623 K in the absence of O_2 yields black crystalline TcOBr_3 as the sole product (CT68, CC68b). It is hydrolyzed by aqueous base to form hydrated TcO_2 and aqueous TcO_4^- (CT68). There are no reports of the preparation of technetium oxoiodides.

Selig and Malm (SM63) prepared TcO_3F by reaction of TcO_2 with flowing F_2 gas at 423 K. The volatile product was isolated as a yellow solid by cooling the vapor, and it was purified by sublimation. A gray residue (not identified) remained behind in the reaction vessel, and it turned red upon exposure to moist air.

TcO₃F melts at 291.4 K and it boils around 373 K (SM63). Vapor pressure measurements were reported for the solid from 264.37 to 291.43 K, and for the liquid from 291.43 to 324.97 K. It is hydrolyzed by aqueous base to form aqueous TcO₄⁻. Reaction of NH₄TcO₄, TcO₂ (BE74), or KTcO₄ (FL82) with anhydrous HF also produces TcO₃F, and addition of AsF₅ to such a solution yields the solid salt [TcO₃⁺][AsF₆⁻] (FL82).

The results of vapor pressure measurements for TcO₃F using a quartz differential Bourdon guage were reported as least-squares equations (SM63). In terms of pressure in bar, these equations become

$$\ln p = (33.556 \pm 0.136) - (7459.0 \pm 37.5)/T$$

for the solid, and

$$\ln p = (24.274 \pm 0.748) - (4753.9 \pm 15.0)/T$$

for the liquid. Reported uncertainty limits are presumed to be one standard deviation. These equations yield an enthalpy of sublimation of 62.1 ± 0.6 kJ·mol⁻¹, an enthalpy of vaporization of 39.5 ± 0.2 kJ·mol⁻¹, and an enthalpy of fusion of 22.5 ± 0.7 kJ·mol⁻¹; these ± values are now 1.96σ.

Binenboym et al. (BE74) reported vibrational frequencies for TcO₃F vapor. They are, ν₁ (Tc-O symmetric stretch) = 962, ν₂ (Tc-F stretch) = 696, ν₃ (O-Tc-O symmetric bend) = 317, ν₄ (Tc-O asymmetric stretch) = 951, ν₅ (O-Tc-O asymmetric bend) = 347, and ν₆ (F-Tc-O rocking motion) = 231 cm⁻¹. Force constants were derived from that study by Baran (B75).

Edwards et al. (EH63b) found that blue TcOF₄ is produced as a byproduct of the direct fluorination of Tc metal. It is similar to ReOF₄ in behavior, and they are isostructural (EJ68). TcOF₄ melts at 407 K (EH63b). Small amounts of a volatile green solid also form during fluorination, and it has been shown to be a trimeric polymorph of the blue colored TcOF₄ (EJ68). This trimer forms hexagonal crystals, space group P6₃/m, with a = (9.00 ± 0.01) × 10⁻¹⁰ and c = (7.92 ± 0.01) × 10⁻¹⁰ m.

Reaction of TcO_3F in anhydrous HF with either XeF_6 or KrF_2 yields a new oxofluoride, and an additional compound is produced after further reaction with KrF_2 (FL82). NMR measurements led to the tentative identification of these compounds as $\text{Tc}_2\text{O}_5\text{F}_4$ and TcO_2F_3 . They were only partially characterized since they were dissolved in HF, but XeF_6 and KrF_2 are such strong oxidizing agents that these two new compounds are undoubtedly Tc(VII) compounds.

Vibrational spectra have been reported for solid, liquid, and gaseous TcO_3Cl (GH-L72, GH-L78), and these vibrational frequencies have been used by Baran (B76) to calculate ideal gas thermodynamic properties of $\text{TcO}_3\text{Cl}(\text{g})$ by using statistical methods. These gas phase vibrational frequencies are (GH-L78) ν_1 (Tc-O symmetric stretch) = 948, ν_2 (Tc-Cl stretch) = 451, ν_3 (O-Tc-O symmetric bend) = 299, ν_4 (Tc-O asymmetric stretch) = 932, ν_5 (O-Tc-O asymmetric bend) = 342, and ν_6 (rocking motion) = 197 cm^{-1} . Electronic transitions occur around 4 170, 16 000, 32 000, and 43 000 cm^{-1} (GH-L78). Baran's calculated values at 298.15 K are $C_{p,m} = 80.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $S_m^\circ = 317.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $H_T^\circ - H_o^\circ = 17.0 \text{ kJ}\cdot\text{mol}^{-1}$, and $G_T^\circ - H_o^\circ = -77.7 \text{ kJ}\cdot\text{mol}^{-1}$.

Müller et al. (MS73) have done a normal coordinate analysis for TcO_3Cl . However, as argued by Binenboym et al. (BE74), the original ν_2 and ν_3 assignments (GH-L72, GH-L78) should be reversed. For TcOBr_3 and TcOCl_3 , only the metal-oxygen stretching frequencies have been reported (CC68b).

There is a lack of thermodynamic data for most of the technetium oxohalides, but, since they hydrolyze in water, they decompose under normal environmental conditions. There is partial thermodynamic data for TcO_3F (experimental, and statistical thermodynamic values could be calculated) and TcO_3Cl (statistical thermodynamic only).

3.3.2 Hydroxohalide Salts

A number of μ -oxobridged dimers have been reported with the general formula $M_4[M_2OX_{10}]$ or their hydrates, where $X = \text{Cl}^-$ or Br^- , $M = \text{NH}_4^+$ or alkali metal cation, and $M' = \text{Ru}(\text{IV})$, $\text{Os}(\text{IV})$, $\text{Re}(\text{IV})$, or $\text{W}(\text{IV})$

(R85). They all contain the same $[X_5M'OM'X_5]^{4-}$ type structural unit. Ziolkowski et al. (ZB62) found that technetium could be co-precipitated with rhenium to form $K_4[(Re,Tc)_2OCl_{10}]$, which is a mixed metal salt of the above type.

When $KTcO_4$ is added to concentrated HCl in the presence of KI, red crystals of a Tc(IV) salt are precipitated from this solution upon cooling. Since technetium and rhenium have many similarities in their chemistry, it is not surprising that this red salt was originally assumed to be $K_4[Tc_2OCl_{10}] \cdot H_2O$ (C65). However, a powder pattern x-ray diffraction study indicated it had a face-centered cubic lattice, rather than the tetragonal lattice expected for a μ -oxobridged dimer. This raised the possibility that this red salt might actually be $K_2[Tc(OH)Cl_5]$, which has the same empirical formula as 1/2 unit of $K_4[Tc_2OCl_{10}] \cdot H_2O$ (C65).

Elder et al. (EF67) prepared crystals of this same red salt by addition of KI to a solution of $KTcO_4$ in $11.3 \text{ mol} \cdot \text{dm}^{-3}$ HCl. A single crystal x-ray structural determination showed this salt was indeed $K_2[Tc(OH)Cl_5]$, which crystallized in the space group $Fm\bar{3}m$ with $a = (9.829 \pm 0.007) \times 10^{-10}$ m and $Z = 4$. It is isostructural with $K_2[TcCl_6]$. As noted by Elder et al., the $m\bar{3}m$ point symmetry indicates that technetium is in a regular octahedral environment. This can only be the case if there is a completely random replacement of Cl^- by OH^- at each octahedral site. Electronic spectra were also reported for $K_2[Tc(OH)Cl_5]$ at room temperature and at liquid air temperature.

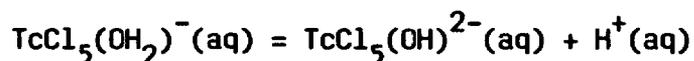
Fergusson et al. (FG83) prepared additional salts of this type by adding various alkali metal chlorides to warm solutions of $NaTcO_4$ in aqueous HCl or HBr. Addition of HI to these solutions, followed by heating the solutions with an IR lamp and then concentrating them, gave the corresponding red hydroxochlorides and brown hydroxobromides of Tc(IV). Powder pattern x-ray diffraction data indicated that all of these salts form cubic lattices, with $a = (9.851 \pm 0.002) \times 10^{-10}$ m for $K_2[Tc(OH)Cl_5]$, $a = (9.964 \pm 0.001) \times 10^{-10}$ m for $Rb_2[Tc(OH)Cl_5]$, $a = (10.315 \pm 0.002) \times 10^{-10}$ m for $Cs_2[Tc(OH)Cl_5]$, and $a = (10.715 \pm 0.003) \times 10^{-10}$ m for $Cs_2[Tc(OH)Br_5]$. Somewhat surprising, these salts do not possess an obvious Tc-OH band in their IR spectra. $K_2[Tc(OH)Cl_5]$ and $Cs_2[Tc(OH)Cl_5]$ are paramagnetic with magnetic moments of 3.6 and 3.5 BM,

respectively (EF67,FG83). When these salts are treated with hot aqueous HCl or HBr, they slowly dissolve to form TcCl_6^{2-} or TcBr_6^{2-} solutions.

Zaitseva et al. (ZK87) prepared crystals of golden-yellow $\text{Zn}[\text{TcCl}_5(\text{OH})]$ by reducing $\text{Zn}(\text{TcO}_4)_2$ with concentrated HCl in the presence of ZnCl_2 . Its identification was based on elemental analyses for Zn, Tc, and Cl; and by IR, EPR, and ^1H NMR. It formed orthorhombic crystals with $a = (9.87 \pm 0.02) \times 10^{-10}$, $b = (6.96 \pm 0.02) \times 10^{-10}$, $c = (7.01 \pm 0.02) \times 10^{-10}$ m, and $Z = 2$. It is isostructural with $\text{M}[\text{Tc}(\text{IV})\text{Cl}_6]$ salts. It was hydrolyzed by water, and it decomposed when heated in an argon atmosphere above 670 K.

Zaitseva et al. (ZK88) also prepared $\text{La}_2[\text{Tc}(\text{OH})\text{Cl}_5]_3$ by heating an aqueous HCl solution of $\text{La}(\text{TcO}_4)_3$ and LaCl_3 . The crystals are orthorhombic with $a = (10.11 \pm 0.02) \times 10^{-10}$, $b = (7.08 \pm 0.02) \times 10^{-10}$, $c = (7.09 \pm 0.02) \times 10^{-10}$ m, and $Z = 2$. This material was paramagnetic, and it was characterized by IR, ESR, ^1H NMR, and thermal analysis.

Koyama et al. (KK68), in their studies of the photochemical aquation of TcCl_6^{2-} , noted that solutions of yellow colored $\text{Tc}(\text{OH}_2)\text{Cl}_5^-$ become brownish if the pH is decreased below 1. They suggested that the reaction

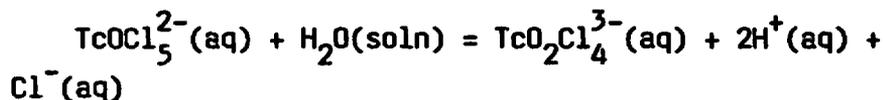


may give rise to this color change. This is the same hydroxochloride formed by the reduction of TcO_4^- in HCl by using HI. Actually, an increase in pH seems more likely to produce acidic dissociation of this type, rather than the claimed decreasing pH.

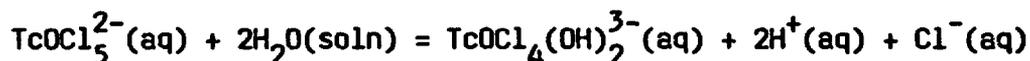
Spitsyn et al. (SG71) studied the progressive hydrolysis of $\text{K}_2[\text{TcOCl}_5]$ in 1.85, 3.7, and 5.5 $\text{mol} \cdot \text{dm}^{-3}$ HCl at room temperature for up to 53 days, and changes the absorption spectra were still occurring even after that time. Hydrolysis of $\text{K}_2[\text{TcOCl}_5]$ in 3 $\text{mol} \cdot \text{dm}^{-3}$ HCl was done both at room temperature and for heated samples. The resulting crystals had a Tc-to-Cl ratio varying from 1:3.8 to 1:4.5. Oxidation with Ce^{4+} showed the technetium valence was Tc(V) in all cases. The varying Tc-to-Cl ratio, and the continuously changing spectra, suggest that a continuous series of hydroxooxochlorides of Tc(V) was being formed.

Crystals of the isolated solid were lustrous brownish-green, and had the approximate empirical composition $K_2[TcOCl_4(OH)]$.

The kinetics of hydrolysis/disproportionation of $TcOCl_5^{2-}$ have been studied in aqueous HCl using spectrophotometry (KG84a), as have the oxidation of this species by HNO_3 (KG84b) and HNO_2 (KG84c). In each case, a rapid equilibrium of the type



or



was invoked in order to explain the observed reaction kinetics. It is impossible to distinguish between these alternate reactions solely on the basis of their kinetic data, so it is not known whether the intermediate species is a hydroxooxo- or a dioxo-complex of tetrachlorotechnetium(V). The equilibrium constant at 298 K for the above reaction (no matter which one is correct) is $K=0.05 \text{ mol}^3 \cdot \text{dm}^{-9}$ at an ionic strength of $I=1 \text{ mol} \cdot \text{dm}^{-3}$ (KG84a), $K=0.06$ at $I=2$, and $K=0.1$ at $I=3$ (KG84c). Extrapolation of $\ln K$ vs. $(I)^{1/2}$ to $I=0$ indicates $K^\circ \sim 0.02 \text{ mol}^3 \cdot \text{dm}^{-9}$. Their values were derived from reaction kinetics measurements. The specific ion interaction approach (our preferred method) gave $K^\circ = 3.6 \times 10^{-4} \text{ mol}^3 \cdot \text{dm}^{-9}$ instead.

Münze (M68a, M75a) studied electrochemical reduction of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ as a function of HCl or HBr concentration, respectively. The reduction at a gold microelectrode was nearly reversible in terms of the change of e.m.f. with pH (M75a). Their claimed reactions are



and



The Tc(III) complexes could be reoxidized to the parent species either electrolytically or by atmospheric oxygen. Redox potential measurements by Hurst (H80) gave $E^{\circ} = 0.23$ V for reduction of the chloride in a $1.2 \text{ mol}\cdot\text{dm}^{-3}$ HCl- $2.65 \text{ mol}\cdot\text{dm}^{-3}$ NaCl mixture, and 0.18 V for reduction of the bromide in $6 \text{ mol}\cdot\text{dm}^{-3}$ HBr. Huber et al. (HH87) reported redox potentials of 0.082 ± 0.004 V for the chloride in $2.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl- $3.0 \text{ mol}\cdot\text{dm}^{-3}$ NaCl and 0.240 ± 0.017 V for the bromide in $2.0 \text{ mol}\cdot\text{dm}^{-3}$ HBr- $3.0 \text{ mol}\cdot\text{dm}^{-3}$ NaBr, relative to the saturated sodium chloride calomel electrode. The redox reactions were reported to involve one electron and to be reversible in all three studies (M75a, H80, HH87). No solid salts of these Tc(III) species have been isolated.

There is a total absence of thermodynamic data for these technetium hydroxohalides. However, the Tc(III) species are sensitive to aerial oxidation, and the Tc(IV) and Tc(V) species probably would undergo extensive or complete hydrolysis (and, possibly disproportionation for Tc(V)) at normal environmental pH values.

3.3.3 Oxohalide Salts

In 1959, Busey (B59a) reported that KTcO_4 was reduced by aqueous HCl to form a singly oxygenated Tc(V) chloro species. The reduction was slow below about $6 \text{ mol}\cdot\text{dm}^{-3}$ HCl, but was quite rapid by about 9-10 $\text{mol}\cdot\text{dm}^{-3}$ HCl. For example, shortly after the KTcO_4 addition, there was 100% Tc(V) formed in $11.86 \text{ mol}\cdot\text{dm}^{-3}$ HCl, 61% in $8.90 \text{ mol}\cdot\text{dm}^{-3}$ HCl, and 0.4% in $6.82 \text{ mol}\cdot\text{dm}^{-3}$ HCl. Addition of H_3PO_2 to the HCl also produced Tc(V). In $12 \text{ mol}\cdot\text{dm}^{-3}$ HCl, this Tc(V) species is slowly reduced to TcCl_6^{2-} . Photolysis of TcCl_6^{2-} in $12 \text{ mol}\cdot\text{dm}^{-3}$ HCl produced a different (and unstable) Tc(V) species.

Busey (B59a) found no evidence for the formation of intermediate species between Tc(VII) and Tc(V) during the reduction of TcO_4^- by HCl. However, the spectroscopic measurements of Ryabchikov and Pozdnyakov (RP64) were interpreted as indicating that TcO_4^- reduction by moderately concentrated HCl occurs by way of a Tc(VI) species, and this Tc(VI) then disproportionates to TcO_4^- and Tc(IV). This disproportionation was found to be slow at room temperature, but was rapid at the boiling point of

the solution. Little reduction of TcO_4^- was observed for HCl concentrations below $7\text{-}7.5 \text{ mol}\cdot\text{dm}^{-3}$, but for $10 \text{ mol}\cdot\text{dm}^{-3}$ and higher HCl the reduction of TcO_4^- went directly to Tc(IV).

Ossicini et al. (OS64) did a chromatographic separation of the products of reaction of TcO_4^- with aqueous HCl and HBr. In each system, the intermediate product of reduction was assumed to be a Tc(V) species, but no direct evidence was obtained for the valence of technetium.

Various claims have been made for the fate of Tc(V) oxochlorides when the HCl is diluted below certain critical concentrations. Busey (B59a) reported that Tc(V) disproportionates into TcO_4^- and Tc(IV) for HCl concentrations below $1 \text{ mol}\cdot\text{dm}^{-3}$. Shukla (S66) reported that hydrolysis of Tc(V) occurs on various chromatographic papers when the HCl concentration drops below $0.6\text{-}2 \text{ mol}\cdot\text{dm}^{-3}$. Shukla's evidence for this was the formation of a black "tail" or spot on the chromatograms (colloid or precipitate?). Spitsyn et al. (SG71) found that the Tc(V) species $[\text{TcOCl}_5]^{2-}$ underwent a slow and progressive hydrolysis to Tc(V)hydroxooxochlorides for HCl concentrations of $3.7 \text{ mol}\cdot\text{dm}^{-3}$ and lower, but for $5.5 \text{ mol}\cdot\text{dm}^{-3}$ and higher concentrations of HCl, Tc(V) is reduced by HCl to Tc(IV). See sect. 3.3.2 for more details. Solvent extraction measurements provide evidence for "hydrolysis" of $[\text{TcOCl}_5]^{2-}$ for HCl concentrations below $3.15 \text{ mol}\cdot\text{dm}^{-3}$ (RM79).

The reduction of TcO_4^- by HCl occurs with the formation of a yellow intermediate stage. Davison et al. (DJ81a) studied the reduction of NH_4TcO_4 in ethanol by aqueous $12 \text{ mol}\cdot\text{dm}^{-3}$ HCl following addition of 2,2'-bipyridine (bpy). A bright yellow solid, with the composition $\text{TcO}_3\text{Cl}[\text{bpy}]$, precipitated within 10 minutes. The corresponding reaction with 48 % HBr rather than concentrated HCl gave yellow-orange $\text{TcO}_3\text{Br}[\text{bpy}]$. Similarly, bright yellow trioxochloro(1,10-phenanthroline)technetium(VII) was prepared by replacing the bpy with phen during reaction. All three of these compounds are insoluble in toluene, methanol, and ethanol, but they are slightly soluble in acetone, methylene chloride, and acetonitrile. All three are hydrolyzed by water to form TcO_4^- . These compounds provide strong circumstantial evidence for the initial formation of $\text{TcO}_3\text{Cl}_n^{-n+1}$ or $\text{TcO}_3\text{Br}_n^{-n+1}$ during reduction of TcO_4^- by HCl or HBr. They (DJ81a) suggested the

actual yellow species was $\text{TcO}_3\text{Cl}_3^{2-}$ by analogy to known rhenium reactions.

Aronson et al. (AH85) found that reduction of TcO_4^- by concentrated HCl is considerably retarded kinetically in the presence of 25 mol·kg⁻¹ choline chloride. The bright yellow color persisted for several hours (in contrast, in the absence of choline chloride, concentrated HCl reduces TcO_4^- to Tc(V) almost instantaneously). The actual yellow intermediate lasted long enough to be characterized spectroscopically. Addition of 2,2'-bipyridine to this solution resulted in the isolation of $\text{TcO}_3\text{Cl}[\text{bpy}]$, which was previously described by Davison et al. (DJ81a).

When TcO_4^- is reduced by HCl in concentrated sulphuric acid, a deep blue solution is obtained and it remains that color for about one hr (KS85b). Measurements of the EPR spectra indicate that a Tc(VI) complex was present, most probably $[\text{TcOCl}_5]^-$. No Tc(VI) oxobromide could be detected when HBr in concentrated H_2SO_4 was used instead of HCl.

Abram et al. (AA86) studied the reaction of solid $[\text{Ph}_4\text{As}]\text{TcO}_4$ with (presumably anhydrous) SOCl_2 and POCl_3 . The reaction with SOCl_2 produced a deep blue solution immediately; in contrast POCl_3 gave a greenish solution that turned deep blue after being kept at 323 K for 20 minutes. The EPR spectra of both blue solutions were nearly identical, although POCl_3 reduction also gave a second species, and the EPR were also very similar to that for the blue solution reported earlier (KS85b) from the reduction of TcO_4^- by HCl in concentrated H_2SO_4 . This indicates that all three systems involve the same Tc(VI) species, probable TcOCl_5^- . According to these authors, the green solution that forms initially from the reaction with POCl_3 probably consists of a mixture of TcOCl_5^- and TcOCl_4 . It is possible, however, that adducts such as $\text{TcOCl}_4 \cdot \text{SOCl}_2$ instead may be present in solutions frozen right after reaction of SOCl_2 with TcO_4^- .

There are a number of studies in which the preparation of solid technetium(V) oxohalides is described, by using reduction of TcO_4^- with HCl or HBr. Jeżowska-Trzebiatowska et al. (J-TW67, J-TN67, BH72) thus prepared $(\text{NH}_4)_2[\text{TcOCl}_5]$, $\text{K}_2[\text{TcOCl}_5]$, and $\text{Cs}_2[\text{TcOCl}_5]$. They

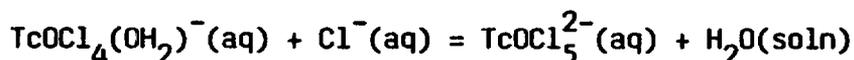
reported IR and UV-visible spectra for these salts, and they made magnetic susceptibility measurements for $(\text{NH}_4)_2[\text{TcOCl}_5]$. This later salt is diamagnetic, at least from 82.5 to 293 K.

Pretz and Peters (PP80b) similarly prepared $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TcOCl}_4]$ and $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TcOBr}_4]$ by reaction of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{TcO}_4$ with concentrated HCl or HBr at room temperature, followed by cooling to 248 K. These two oxohalides are nearly insoluble in aqueous acids, but they are soluble in organic solvents. Raman spectra were reported for the solid salts. Thomas et al. (TD80a) prepared $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TcOBr}_4]$ by dissolving KTcO_4 in 48 % HBr at 273 K, followed by addition of aqueous $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$. IR spectra were measured and compared to the corresponding oxochloride and oxoiodide salts. Thomas et al. (TH85) used a similar procedure to prepare $\text{Cs}_2[\text{TcOCl}_5]$ and $\text{Cs}_2[\text{TcOBr}_5]$. $[(\text{CH}_3\text{CH}_2)_4\text{N}]_2[\text{TcOCl}_5]$ was prepared from $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{TcOCl}_5]$ by ligand exchange in CH_2Cl_2 at room temperature. Lower temperatures of around 273 K are advantageous for preparation of technetium(V)oxobromides in order to reduce the amount of Tc(IV) formed by further reduction of Tc(V) by HBr. The vibrational spectra of $\text{K}_2[\text{TcOCl}_5]$, $\text{Cs}_2[\text{TcOCl}_5]$, and $\text{Cs}_2[\text{TcOBr}_5]$ have been analyzed in detail by Hanuza et al. (HJ-T87).

Reduction of TcO_4^- to Tc(IV) by HI is quite rapid at room temperature but, by cooling the solutions in an isopropyl alcohol/dry ice bath, $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TcOI}_4]$ was obtained (TD80a). The IR spectrum of $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TcOI}_4]$ in Nujol was reported. A method that gives this same dark golden-brown material but in a purer form is ligand exchange of $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TcOCl}_4]$ with NaI in acetone (PP81). This eliminates contamination with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{I}_3$ that occurs when HI reduction is used (PP80b).

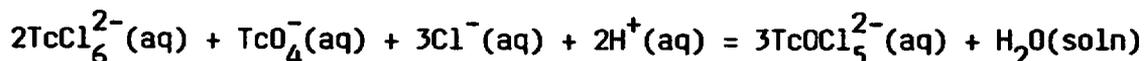
Cotton et al. (CD79) used reduction of TcO_4^- by concentrated HCl and H_3PO_2 to prepare both gray-green $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TcOCl}_4]$ and dark green $[(\text{Ph}_3\text{P})_2\text{N}][\text{TcOCl}_4]$. A detailed single crystal x-ray study was done for the latter compound: it crystallizes in the orthorhombic space group $\text{Pna}2_1$ with $a=(21.618\pm 0.005) \times 10^{-10}$, $b=(16.870\pm 0.005) \times 10^{-10}$, $c=(9.658\pm 0.003) \times 10^{-10}$ m, and $Z=4$. The TcOCl_4^- ion has a distorted square pyramidal structure and C_{2v} symmetry.

From the above information about technetium(V) oxohalides, it appears that precipitation with bulkier cations generally yield TcOX_4^- salts, whereas smaller and intermediate sized cations yield TcOX_5^{2-} salts. Measurements have been made for the equilibrium constant of

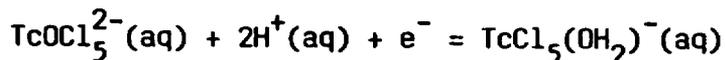


in aqueous HCl using Raman spectroscopy (TH85). At room temperature and 12 $\text{mol}\cdot\text{dm}^{-3}$ HCl, the equilibrium constant is $K=0.0015\pm 0.0010$ $\text{mol}^{-1}\cdot\text{dm}^3$. This establishes that TcOCl_4^- is by far the dominant Tc(V) species in these solutions. Since TcOCl_5^{2-} salts form when precipitation is done with smaller cations, this implies that their corresponding TcOCl_4^- salts are much more soluble than TcOCl_5^{2-} salts in 12 $\text{mol}\cdot\text{dm}^{-3}$ HCl. The opposite must be true for larger cations of the type $[\text{n}-(\text{C}_4\text{H}_9)_4\text{N}]^+$ and $[(\text{Ph}_3\text{P})_2\text{N}]^+$. In contrast, results from liquid-liquid extraction of Tc(V) by tributylphosphate suggest that TcOCl_5^{2-} is an important species when $[\text{H}^+] = 3.15$ to 6 $\text{mol}\cdot\text{dm}^{-3}$ and $[\text{Cl}^-] > 6$ $\text{mol}\cdot\text{dm}^{-3}$ (RM79).

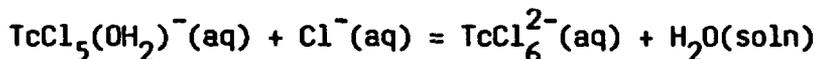
It was reported that TcO_4^- and TcCl_6^{2-} react together slowly in 1.2 $\text{mol}\cdot\text{dm}^{-3}$ HCl to form Tc(V) oxochlorides (OS64). After 43 hours 9 % Tc(V) had formed, and this increased to 12 % after 67 hours. A much more detailed study of the reproporationation of TcO_4^- and TcCl_6^{2-} was done by Koltunov and Gomonova (KG85). A preliminary experiment indicated no detectible reaction occurred between TcO_4^- and TcCl_6^{2-} below room temperature, but at 353 K the reaction occurs at a significant rate. The reaction kinetics were studied at ionic strengths of 1 to 4 $\text{mol}\cdot\text{dm}^{-3}$ and from 348 to 363 K using spectrophotometry. The observed reaction was



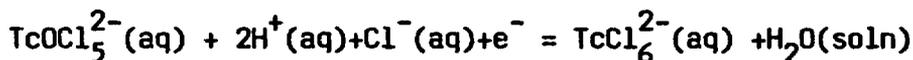
Rajec and Macávek (RM81) studied the kinetics of electrolytic reduction of TcOCl_5^{2-} in 4.0 $\text{mol}\cdot\text{dm}^{-3}$ HCl by using simultaneous coulometry and UV-visible spectrophotometry. The observed reaction sequence was



followed by



It is also possible that some of the TcOCl_5^{2-} was directly reduced in a single step of the type



Busey (B59a) found that the initial reduction of TcO_4^- by HCl was to Tc(V) and it was strongly dependent on HCl concentration; this study was described earlier in this section. In contrast, at 373 K, Jeżowska-Trzebiatowska and Bażuka (J-TB65) found that TcO_4^- was directly reduced to Tc(IV) by $12 \text{ mol} \cdot \text{dm}^{-3}$ HCl.

Several studies have been published in which paper chromatography has been used to separate TcO_4^- from the products of its reduction by HCl or HBr, and the relative amounts of various reduced forms of technetium were determined (OS64, S66, WD71, S71a, S71b, S78, dLW82). In general, in these studies it was assumed that TcO_4^- was first reduced to one or more Tc(V) oxohalide, with subsequent reduction to Tc(IV) halides generally also being "observed". Chromatographically separated peaks were then assigned to TcO_4^- and to one or more Tc(V) and Tc(IV) species. However, as noted by de Liverant and Wolf (dLW82), there are no direct measurements that allow an unambiguous assignment of the technetium valence to the reduction products. Since salts of TcOCl_4^- and TcOCl_5^{2-} have both been isolated from solutions prepared in a similar manner, and both species have been spectroscopically identified in solution, the formation of similar Tc(V) species will be assumed in interpreting chromatographic data. This generally agrees with the interpretations given in the various published studies.

Ossicini et al. (OS64) found that TcO_4^- was rapidly reduced by concentrated HCl at 373 K, but some Tc(V) was still present even after 4 hours. This conclusion conflicts with that of Jeżowska-Trzebiatowska and Bażuka (J-TB65) who found that TcO_4^- was directly reduced to Tc(IV) under these conditions. At room temperature, Ossicini et al. (OS64) reported that TcO_4^- was reduced by concentrated HBr to Tc(IV) with a

Tc(V) intermediate stage. No Tc(V) could be detected after one day reaction with "concentrated" HBr, and no Tc(V) remained after 3 days for 80 % HBr. With 60 % HBr, no formation of Tc(V) was observed until after about 3 days, and with 40 % HBr no reaction was observed at all in this time frame. The extent of formation of Tc(V) from TcO_4^- as a function of HCl concentration used for reduction has been described in some detail (S66, WD71). A recent spectrophotometric study (T-CI88) has been published, in which the initial stage of the reduction of TcO_4^- by concentrated HBr was found to occur too rapidly to be quantitatively studied, but it was possible to do the kinetic studies in $6 \text{ mol}\cdot\text{dm}^{-3}$ HBr. Crystals of $[(\text{CH}_3\text{CH}_2)_4\text{N}][\text{TcOBr}_4\cdot\text{H}_2\text{O}]$ were isolated from this reaction of TcO_4^- with concentrated HBr.

Shukla (S71a) found that adding NaCl to the HCl retards reduction of TcO_4^- ; in contrast, addition of LiCl increases the reduction rate. However, when LiCl was present at $12 \text{ mol}\cdot\text{dm}^{-3}$ in the absence of HCl, no reduction of TcO_4^- occurred even after 40 days. Thus, the present of both H^+ and halide in large amounts is essential for reduction of TcO_4^- . This can be seen from the reaction stoichiometry



Shukla (S71b) studied the effect of adding small amounts of Br^- or I^- to HCl on the extent and rate of reduction of TcO_4^- . Measurements were done at room temperature with $7 \text{ mol}\cdot\text{dm}^{-3}$ HCl. Shukla found that $7 \text{ mol}\cdot\text{dm}^{-3}$ HCl by itself only reduced a small percentage of TcO_4^- to Tc(V) even after three days, and only about 21 % was reduced to Tc(V) after four months. In contrast, addition of small amounts of Br^- to this HCl caused complete reduction of TcO_4^- to Tc(V) after about 45 minutes, and all Tc(V) was further reduced to Tc(IV) after about 3 days. When I^- was added to this HCl, then TcO_4^- was completely and instantaneously reduced to Tc(IV). In fact, this is the favored method for preparing $\text{Tc}(\text{OH})\text{Cl}_5^{2-}$ salts, as was discussed in sect. 3.3.2.

Shukla (S71c) studied the oxidation of TcCl_6^{2-} to TcO_4^- by H_2O_2 and Cl_2 in aqueous $0.6 \text{ mol}\cdot\text{dm}^{-3}$ HCl. This oxidation by Cl_2 occurred by way of a Tc(V) intermediate stage, but H_2O_2 slowly oxidized TcCl_6^{2-} directly to TcO_4^- .

Information obtained from the studies cited above indicates that: 1) The rates of reduction of TcO_4^- by halides in acid solution follow the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$. In addition, I^- reduces TcO_4^- directly to $\text{TcX}_5(\text{OH})^{2-}$ in HCl or HBr solutions except at reduced temperatures. The rates of the subsequent reduction of Tc(V) to Tc(IV) follow the order $\text{Br}^- > \text{Cl}^-$. 2) Reduction rates for TcO_4^- by HCl or HBr increase as the acid concentration is increased. 3) Increasing the reaction temperature increases the rate at which TcO_4^- is reduced to Tc(V) by HCl or HBr, and it also increases the rate at which Tc(V) is reduced to Tc(IV).

The above studies were done by using ^{99}Tc , and the observed reactions are predominantly or entirely due to chemical causes, since ^{99}Tc has a sufficiently long half-life ($t_{1/2} = 2 \times 10^5$ yr) that radiolytic effects should be of secondary importance. However, ^{99}Tc is frequently prepared by irradiation of molybdenum or molybdenum compounds with neutrons to produce ^{99}Mo , which in turn decays to $^{99\text{m}}\text{Tc}$. This $^{99\text{m}}\text{Tc}$ then decays to its ground state $^{99\text{g}}\text{Tc}$ ($= ^{99}\text{Tc}$) with $t_{1/2} = 6.0$ hr by emitting a monoenergetic gamma ray. The resulting gamma ray flux produces radiolysis of water and the technetium species. Because of their high reactivity, these radiolytically generated species can have major effects on the reaction between TcO_4^- and HCl (S78, dLW82, CV71).

Cifka and Veselý (CV71) studied $^{99\text{m}}\text{Tc}$ generators, which are prepared by absorbing ^{99}Mo on a column (frequently of alumina). The $^{99\text{m}}\text{Tc}$ resulting from radioactive decay of ^{99}Mo is then eluted with NaCl. Cifka and Veselý were unable to uniquely determine the mechanism for the reduction of TcO_4^- involving radiolysis. However, they found that if TcO_4^- is exposed to gamma rays from ^{60}Co , then it is changed into a species that is strongly absorbed on alumina; this may well be a Tc(IV) species.

A more detailed study was done by Shukla (S78), who studied the reduction of $^{99\text{m}}\text{TcO}_4^-$ by concentrated HCl at various temperatures. Shukla noted that "chromatographically pure" $^{99}\text{Tc(V)}$ was obtained by reaction of $^{99}\text{TcO}_4^-$ with concentrated HCl at 273 K, but about 2 yrs was required to form "chromatographically pure" Tc(IV) under these conditions. In contrast, the reduction of $^{99\text{m}}\text{TcO}_4^-$ to $^{99\text{m}}\text{Tc(V)}$ in

concentrated HCl, and the subsequent reduction of $^{99m}\text{Tc(V)}$ to $^{99m}\text{Tc(IV)}$ was much more rapid than for ^{99}Tc . Chromatographically pure $^{99m}\text{Tc(IV)}$ was obtained within 48 hrs by using ^{99m}Tc . Noll and Münze (NM75) found that $^{99m}\text{TcO}_4^-$ was reduced by HCl directly to TcCl_6^{2-} , in contrast to $^{99}\text{TcO}_4^-$ for which they observed Tc(V) as an intermediate (presumably at room temperature). This Tc(V) then disproportionated to TcCl_6^{2-} and TcO_4^- .

A further study by de Liverant and Wolf (dLW82) showed that $^{99m}\text{TcO}_4^-$ (relative to $^{99}\text{TcO}_4^-$) was reduced to lower valence technetium species at lower HCl concentrations and even in neutral or alkaline solutions; these are conditions under which $^{99}\text{TcO}_4^-$ undergoes little or no reduction. Thus, technetium in concentrated radioactive wastes may undergo chemical reactions not generally observed at lower radiation fluxes.

No thermodynamic data are available for any of the salts described in this section; however their aqueous solutions disproportionate, hydrolyze, or are oxidized by atmospheric air under normal environmental conditions.

4. Chalcogen Compounds and Complexes

4.1 Sulphur Compounds and Complexes

4.1.1 Sulphur Compounds

Addition of H_2S to $0.5\text{--}5.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl solutions of TcO_4^- yielded "complete precipitation" of a technetium sulphide. In $10 \text{ mol}\cdot\text{dm}^{-3}$ HCl only a small fraction of technetium precipitated, in contrast to rhenium which had more complete precipitation under this condition (PS39). The solid compound was dark black and had the chemical formula Tc_2S_7 (RM52,CN52). The initial precipitate can contain up to 20 % excess sulphur, which can be removed by extraction with CS_2 (RM52). Tc_2S_7 can also be prepared by treatment of acidic TcO_4^- solutions with sodium thiosulphate (EL77), and thioacetamide can similarly be used (A60). Trace amounts of technetium can be co-precipitated as sulphides with certain second and third row transition metals (A60).

Tc_2S_7 that was heated to as low as 373 K in a Cl_2 stream

reportedly was completely volatilized, and condensed solids collected in the cooler parts of the reaction tube (PS39). The Cl_2 apparently functions as a carrier gas for vapor phase transport. Simply heating Tc_2S_7 in the absence of O_2 yields amorphous TcS_2 (B59b). Crystalline TcS_2 was prepared by chemical transport along a temperature gradient in a sealed tube, with temperatures of 1423 and 1353 K at the two ends of the tube. An excess of sulphur, along with Cl_2 , Br_2 , or I_2 as a carrier gas, improved transport (WJ71). TcS_2 forms triclinic crystals with $a = 6.465 \times 10^{-10}$, $b = 6.375 \times 10^{-10}$, $c = 6.659 \times 10^{-10}$ m, $\alpha = 103.61^\circ$, $\beta = 62.97^\circ$, and $\gamma = 118.96^\circ$. Its structure is probably a distorted $\text{Cd}(\text{OH})_2$ -type cell. Differential thermal analysis experiments give no evidence for a structural change between 93 and 1423 K.

McDonald and Cobble (MC62) measured combustion enthalpies for several rhenium sulphides, and used these results to estimate $\Delta_f G_m^\circ$, $\Delta_f H_m^\circ$, and S_m° for TcS_2 , TcS_3 , and Tc_2S_7 . No direct thermodynamic data are available for these technetium sulphides. In addition, there are no reports of the preparation of TcS_3 , so we will not consider it further. Their estimated values are (with $\pm 1.96\sigma$)

$$\Delta_f H_m^\circ = -223.8 \pm 41.0 \text{ kJ}\cdot\text{mol}^{-1}, \Delta_f G_m^\circ = -215.9 \pm 42.1 \text{ kJ}\cdot\text{mol}^{-1}, \text{ and } S_m^\circ = 71.1 \pm 31.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ for } \text{TcS}_2(\text{cr});$$

$$\text{and } \Delta_f H_m^\circ = -615.0 \pm 57.4 \text{ kJ}\cdot\text{mol}^{-1}, \Delta_f G_m^\circ = -580.5 \pm 60.4 \text{ kJ}\cdot\text{mol}^{-1}, \text{ and } S_m^\circ = 175.7 \pm 63.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ for } \text{Tc}_2\text{S}_7(\text{cr}).$$

4.1.2 Oxosulphur Complexes

Constant current electrolysis and potentiostatic reductions were performed for dilute aqueous TcO_4^- in the presence of SO_4^{2-} , but no details were provided. Both Tc(III) and Tc(IV) could be obtained, and spectroscopic evidence was found for complexes with sulphate in both cases (PL82). Spitsyn et al. (SK76) separated a non-colloidal brown complex of technetium, prepared by electrolysis of TcO_4^- in aqueous H_2SO_4 , using electrophoresis. Oxidation of this complex to TcO_4^- in solution, by use of Ce(IV) sulphate, indicated a $3e^-$ change, so Tc(IV) was present in the brown complex. Based on absorption spectrum measurements as a function of pH, they suggested the brown complex was $[\text{Tc}(\text{OH})_2(\text{SO}_4)_2]^{2-}$ (SK76). Ianovici et al. (IK81) studied photolysis of $0.005 \text{ mol}\cdot\text{dm}^{-3} \text{ TcCl}_6^{2-}$ in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{SO}_4$, and

isolated a pink cationic complex and a neutral species using low-voltage electrophoresis. Photolysis of $10^{-3} \text{ mol}\cdot\text{dm}^{-3} \text{ TcBr}_6^{2-}$ in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{SO}_4$ gave small amounts of pink and orange cationic species, larger amounts of a brown-orange neutral species, and a yellow anionic species (CI88). Electrolysis of $0.006 \text{ mol}\cdot\text{dm}^{-3} \text{ NH}_4\text{TcO}_4$ in $1 \text{ mol}\cdot\text{dm}^{-3} (\text{NH}_4)_2\text{SO}_4$ with added H_2SO_4 also gave either pink or brown solutions, with pink solutions usually (but not always) obtained at $\text{pH} = 0.5-1.5$ (VH67).

When TcO_4^- is reduced by SnCl_2 in the presence of potassium ferrocyanide and H_2SO_4 , a transient blue species forms which then turns reddish-violet. After some time a dark violet compound, of uncertain composition, is precipitated (A-KM62).

Several polarographic studies have been made for TcO_4^- reduction in H_2SO_4 and in alkaline SO_4^{2-} solutions. Reduction potentials for TcO_4^- in $0.25 \text{ mol}\cdot\text{dm}^{-3} \text{ K}_2\text{SO}_4$, with H_2SO_4 or KOH added to obtain $\text{pH} = 4$ to 13, are essentially identical to the potentials for the first two reduction waves of TcO_4^- in KCl at these pH values (SR63). This implies that SO_4^{2-} complexes of Tc(IV) and Tc(III) are weak or non-existent at $\text{pH} \geq 4$ owing to competition from hydrolysis. However, the second reduction wave appears to be an absorption postwave (SR63, GD79).

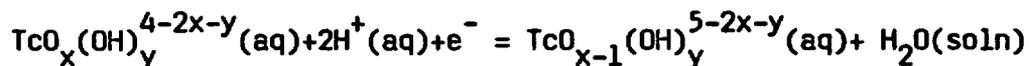
Polarographic reduction of TcO_4^- in NaHSO_4 - Na_2SO_4 mixtures at $\text{pH} \sim 1$ to 4 gives three reduction waves, with the first two being irreversible (SR63, GD79, RC78). The first reduction wave is $4e^-$ to Tc(III) , the second is apparently $7e^-$ for TcO_4^- to metallic Tc , and the third is a catalytic hydrogen discharge wave. The first two waves are diffusion controlled, and the second has a maxima.

The polarographic behavior of TcO_4^- in aqueous Na_2SO_4 and Na_2SO_4 - H_2SO_4 mixtures is very similar to its behavior in ClO_4^- and HClO_4 solutions (ZK70). This implies that reduced forms of technetium complex little with sulphate. Cyclic voltammetry of TcO_4^- in $0.5-1.5 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{SO}_4$ gives anodic and cathodic peaks that involve Tc(III) and Tc(IV) hydrous oxides; these potentials are concordant with results in HCl , HClO_4 , NaOH , and other ionic media (MM74). No well defined polarographic reduction waves are observed in $2-10 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{SO}_4$

(MS59, MK60).

Since none of the reduction waves for TcO_4^- in H_2SO_4 or NaHSO_4 - Na_2SO_4 are reversible, and the nature of sulphate complexes of technetium not completely certain, no useful thermodynamic data can be derived from these reduction potentials. In addition, no solid technetium sulphates or other oxysulphates have been characterized.

The half-wave potential for oxidation of Tc(III) in NaHSO_4 - Na_2SO_4 changed linearly with pH, for pH about 1.6-3.0, and it was quasi-reversible (GD79). This potential can be used to relate the Gibbs energy of aqueous Tc(IV) to Tc(III) provided 1) sulphate complexes are negligible, and 2) an assumption is made as the hydrolysis state of Tc(IV). This redox reaction has the form



where $(x=1, y=0)$, $(x=1, y=1)$, and $(x=1, y=2)$ are possible combinations, and $E^\circ = 0.319 \text{ V}$ in $0.5 \text{ mol} \cdot \text{dm}^{-3}$ NaHSO_4 - Na_2SO_4 solutions.

Colton and Tomkins (CT68) evaporated an aqueous NH_4TcO_4 solution to dryness and then added an excess of thionyl chloride (SOCl_2). After 2 days the red solution was removed and the orange solid was "pumped dry" to remove excess SO_2Cl_2 . This orange solid was hydrolyzed by water to form two $\text{TcO}_4^-(\text{aq})$ for each hydrated TcO_2 , which indicated that the original orange solid contained Tc(VI). This information, together with analyses for the amounts of Tc and Cl^- present, suggests that the solid was the adduct $[\text{NH}_4]_2[\text{TcO}_2\text{Cl}_4] \cdot \text{SO}_2\text{Cl}_2$.

Abram et al. (AA86) reacted $[\text{Ph}_4\text{As}]\text{TcO}_4$ with anhydrous SOCl_2 and obtained a deep blue solution containing Tc(VI). They interpreted the EPR spectra of its frozen solutions as containing TcOCl_5^- , but acknowledged that an adduct such as $\text{TcOCl}_4 \cdot \text{SOCl}_2$ was an alternate possibility.

4.2 Other Chalcogen Compounds and Complexes

Very little information is available for the selenides and tellurides of technetium. Reaction of technetium with these chalcogens in a sealed reaction tube

with a temperature gradient, and with Br₂ or I₂ as carriers, gave chemical transport of TcSe₂ or TcTe₂ to form crystals at the cool end of the tube. Temperatures at the ends of the tube were 1353 and 1273 K for the selenide, and 1253 and 1113 K for the telluride (WJ71).

Single crystal x-ray determination for TcTe₂ showed this compound to have monoclinic symmetry with $a = 12.522 \times 10^{-10}$, $b = 7.023 \times 10^{-10}$, $c = 13.828 \times 10^{-10}$ m, $\alpha = 90^\circ$, $\beta = 101.26^\circ$, and $\gamma = 90^\circ$ (WJ71). The shape of the unit cell was said to resemble high-temperature MoTe₂, but with a doubling of the a and b axes lengths. TcSe₂ seemed to be isostructural with TcS₂, but the diffraction spots were too diffuse to allow determination of unit cell parameters. No thermodynamic data are available for TcSe₂ or TcTe₂.

A mixed sulphur-selenium complex has been reported (SJ81), [(CH₃CH₂)₄N]TcOL₂, where L represents $\left[\begin{array}{c} \text{Se} \\ \text{S} \end{array} \right] \text{C} = \text{C} \begin{array}{c} \text{CN} \\ \text{CN} \end{array} \right]^{2-}$. This is, as formulated, a Tc(V) complex. The complex was partially characterized by C, H, and N analyses, and by IR and UV-visible spectra. It was prepared by ligand exchange with the technetium gluconate complex in the presence of [(CH₃CH₂)₄N]Br. The gluconate complex had been prepared by reduction of NH₄TcO₄ with SnCl₂ in 0.1 mol·dm⁻³ HCl containing sodium gluconate.

Abram et al. (AS85) prepared nitrido complexes of the type [TcNL₂]⁰ where L = $\left[\begin{array}{c} \text{Se} \\ \text{Se} \end{array} \right] \text{C} - \text{N} \begin{array}{c} \text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{CH}_3 \end{array} \right]^-$ or $\left[\begin{array}{c} \text{Se} \\ \text{S} \end{array} \right] \text{C} - \text{N} \begin{array}{c} \text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{CH}_3 \end{array} \right]^-$. They were prepared by using ligand exchange with TcNCl₂(Ph₃P)₂ in an acetone-ethanol mixture. Both contain the Tc≡N²⁺ group. Hieber et al. (HO68a) prepared a compound that they formulated as [Tc(CO)₃Se(Ph)₂Cl]₂, by reaction of Tc(CO)₅Cl with diphenyl selenide Ph₂Se. This technetium complex melts at 466 K.

5. Pnictide Compounds and Complexes

5.1.1 Nitrogen (Nitride and Nitrido) Compounds

When powdered technetium, prepared by hydrogen reduction of NH₄TcO₄, was heated to 670-1170 K in a nitrogen atmosphere no reaction occurred (TR64). However, powdered technetium reacted with ammonia at 970-1370 K to produce a

face centered cubic phase TcN_m where $m \leq 0.76$ with lattice constant $a = (3.980-3.985) \times 10^{-10}$ m. They suggested that the "ideal" phase could actually be TcN with a NaCl-type structure (TR64). Thermal decomposition of NH_4TcO_4 in argon yielded TcO_2 , but when NH_4TcO_4 was heated to 570 K in a NH_3 -Ar mixture, a nitride was produced (VK78a).

Thermal decomposition of $(NH_4)_2TcCl_6$ in argon began at 633 K and was complete by 732 K; for $(NH_4)_2TcBr_6$ decomposition began at 643 K and was complete by 757 K. A nitride phase was produced by their thermal decomposition; it had the composition $TcN_{0.75}$ with $a=3.980 \times 10^{-10}$ m, but when this $TcN_{0.75}$ was heated to 770 K almost no nitrogen remained and $a=3.954 \times 10^{-10}$ m (VK78b, VZ83). Heating to even higher temperatures yielded technetium metal. The corresponding thermal decomposition of $(NH_4)_2TcI_6$ yielded only metallic technetium (VK81). Similarly, the thermal decomposition of $(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$ in argon or argon-helium mixtures produced "TcN", around 673-733 K, with a unit cell parameter of $a = (3.945 \pm 0.001) \times 10^{-10}$ m (SK87).

TcN_m is black, brittle, and insoluble in 30 % H_2O_2 -concentrated alkali. It does dissolve in warm concentrated nitric acid (VK78b). No thermodynamic data are available.

Thermal decomposition of $(NH_4)_2TcF_6$ in argon (presumably, above 570 K) was studied by thermogravimetric analysis (LS66); a weight loss of 46.5 % was observed. Reduction of this residue with H_2 to technetium metal at 773 K then gave an additional weight loss of 25.5 %. These weight loss values are consistent with the residue being "TcNF". Powder pattern data indicated a hexagonal unit cell with $a = 5.98 \times 10^{-10}$ and $c = 3.80 \times 10^{-10}$ m; in contrast (surprisingly) with $ReNF$, which has a tetragonal unit cell. In addition, Spitsyn et al. (SK87) suggested that thermal decomposition of $(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$ in argon or argon-helium mixtures yielded thermally unstable $TcNCl$ around 633-723 K; it readily decomposed to "TcN" at higher temperatures.

If NH_4TcO_4 is dissolved in concentrated aqueous HCl or HBr in the presence of sodium azide NaN_3 , then air-stable salts of $TcNCl_4^-$ or $TcNBr_4^-$ are obtained (BB84). These tetrahalonitridotechnetate(VI) salts contain a $Tc \equiv N$ triple bond, with technetium in the unusual hexavalent state. The tetraphenylarsonium salts $[AsPh_4][TcNX_4]$ are isostructural with each other and with other transition metal salts of the same type. The crystals are

tetragonal with space group $P4/n$ and $Z=2$. For the chloride salt, $a=(12.707\pm 0.002) \times 10^{-10}$ and $c=(7.793\pm 0.001) \times 10^{-10}$ m; for the bromide salt, $a=(12.875\pm 0.002) \times 10^{-10}$ and $c=(7.992\pm 0.001) \times 10^{-10}$ m. These structures contain discrete AsPh_4^+ and TcNX_4^- units, with the four halide ligands possessing ideal C_{4v} symmetry. The $\text{Tc}\equiv\text{N}$ bond length is $(1.581\pm 0.005) \times 10^{-10}$ in $[\text{AsPh}_4][\text{TcNCl}_4]$, and $(1.596\pm 0.006) \times 10^{-10}$ m in $[\text{AsPh}_4][\text{TcNBr}_4]$. Tetra-n-butylammonium salts were also prepared (BB84, BB85).

The halide ligands are somewhat labile in these nitrido compounds. Addition of $[\text{AsPh}_4][\text{TcNCl}_4]$ to LiBr in acetone yielded $[\text{AsPh}_4][\text{TcBr}_4]$ (BB86). Samples prepared with CsCl rather than $[\text{AsPh}_4]\text{Cl}$ gave air-stable $\text{Cs}_2[\text{TcNCl}_5]$ (BB86). Mixtures of $[\text{AsPh}_4][\text{TcNCl}_4]$ and $[\text{AsPh}_4][\text{TcNBr}_4]$ that are dissolved in acetonitrile and boiled for 0.5 hr yield $[\text{AsPh}_4][\text{TcNBr}_{4-p}\text{Cl}_p]$ salts (KS86).

The salts $[\text{AsPh}_4][\text{TcNX}_4]$ and $\text{Cs}_2[\text{TcNCl}_5]$ are readily hydrolyzed by water to form violet-purple solutions with gradual precipitation of a brown solid. This solid has not been identified, but it contains the $\text{Tc}\equiv\text{N}$ group (BB86). The TcNCl_4^- anion is reduced by PPh_3 , KNCS , $\text{Na}[\text{S}_2\text{CNet}_2]$, and 8-quinolinethiol to yield $\text{Tc}\equiv\text{N}$ complexes of Tc(V) . Mixtures of NH_4TcO_4 with $0.5 \text{ mol}\cdot\text{dm}^{-3}$ HCl in aqueous ethanol with added PPh_3 are reduced by $\text{N}_2\text{H}_4\cdot 2\text{HCl}$ to $\text{Tc(V)NCl}_2(\text{PPh}_3)_2$ directly (KL81).

Solutions of $\text{Cs}_2[\text{TcNCl}_5]$ in aqueous HCl have been studied by Baldas and Boas (BB88). In $5.6 \text{ mol}\cdot\text{dm}^{-3}$ HCl the predominant species is yellow $[\text{TcNCl}_4]^-$. Dissolution of $\text{Cs}_2[\text{TcNCl}_5]$ in H_2O gave a brown precipitate; dissolution of this precipitate in HCl then gave a pink solution, but further addition of HCl gave an intense blue solution that turned yellow after about one hour. In $1.25 \text{ mol}\cdot\text{dm}^{-3}$ HCl at equilibrium, about 66% of the Tc(VI) was present as the pink species. Magnetic susceptibility and ESR measurements indicated the pink and blue species are diamagnetic. This information, together with optical spectroscopy measurements on these solutions, led the authors to conclude that the pink and blue species were probably dimers of $[\text{TcNCl}_x]^{3-x}$, with different numbers of chlorides and bridging oxygens.

Abram et al. (AS85) give references for the preparation of many $[\text{Tc(V)}\equiv\text{N}]^{2+}$ complexes with organic ligands. These complexes are soluble in CH_2Cl_2 ,

CHCl_3 , benzene, and acetone, but they are nearly insoluble in water and hydrocarbons. Upon addition of excess Cl_2 or Br_2 to their solutions at 323 K, these complexes are converted to $[\text{Tc(VI)}\equiv\text{N}]^{3+}$ halide complexes without affecting the $\text{Tc}\equiv\text{N}$ bond. In all cases, oxidation with Cl_2 was reported to give $[\text{TcNCl}_5]^{2-}$.

No evidence was found for TcNX_5^{2-} in non-aqueous or concentrated aqueous HX solutions in another study, even when TcNX_4^- salts are in the presence of a 2000 fold halide ion excess (BB87). In aqueous acidic solutions the likely predominant species is $\text{TcN}(\text{OH}_2)\text{X}_4^-$.

Baldas et al. (BC88) have prepared a somewhat complicated nitrido complex of technetium(VI) by reaction of aqueous oxalic acid and a solution of $[\text{Ph}_4\text{As}][\text{TcNCl}_4]$ in acetone. Red-brown crystals gradually formed from this solution, and they were partially characterized by elemental analysis and IR. A single crystal structural determination indicates this complex is tetraphenylarsonium cyclo-bis- $\{\mu\text{-(oxalato-}0,0'0'',0''')\text{-}\mu\text{-oxo-bis[nitrido-oxalatotechnetate(VI)]}\}$, $[\text{Ph}_4\text{As}]_4[\text{Tc}_4\text{N}_4\text{O}_2(\text{ox})_6]$. It crystallized in the monoclinic space group $\text{P2}_1/\text{n}$ with $a = (14.433 \pm 0.001) \times 10^{-10}$, $b = (13.229 \pm 0.001) \times 10^{-10}$, $c = (27.020 \pm 0.001) \times 10^{-10}$ m, $\alpha = 90^\circ$, $\beta = 92.90 \pm 0.01^\circ$, $\gamma = 90^\circ$, and $Z = 4$. Each technetium atom is coordinated with five oxygen atoms and one nitrogen to form a distorted octahedron. This complex decomposes when heated in air at 523-528 K. Addition of thionyl chloride to the complex converts it back to $[\text{Ph}_4\text{As}][\text{TcNCl}_4]$.

No thermodynamic data are available for these nitrido compounds, but they are unlikely to form under normal environmental conditions. However, if they are formed, they are likely to persist since the $\text{Tc}\equiv\text{N}$ group is very stable against chemical attack, even when it undergoes oxidation-reduction ($\text{TcN}^{2+}/\text{TcN}^{3+}$) or ligand substitution reactions.

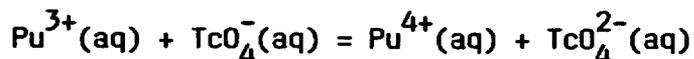
5.1.2 Nitrogen Complexes

This section is concerned with nitrogen complexes of technetium. Elsewhere in this book we have discussed other nitrogen containing compounds and complexes: nitride and nitrido compounds (sect. 5.1.1); cyanides,

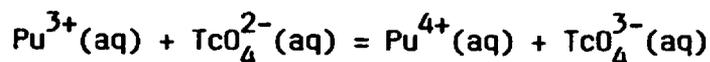
oxocyanides, isothiocyanates, and oxoisothiocyanates (sect. 10.2); and nitrosyl complexes (sect. 10.3). In addition, most of the reported ammonia complexes of technetium are nitrosyl complexes (sect. 10.3). In this section we are concerned with the remaining complexes of technetium containing inorganic nitrogen ligands: nitrates and nitrites, ammonia (in the absence of nitrosyl), hydrazine, and molecular nitrogen complexes.

Reprocessing of fuel rods from nuclear reactors generally involves dissolution of these rods in HNO_3 or nitrate solutions. Both HNO_3 and aqua regia dissolve technetium metal to form TcO_4^- solutions (A60,SK65). In addition, HNO_3 oxidized uncomplexed Tc(IV), TcCl_6^{2-} (A60, G56), and Tc(V) oxochlorides (KG84b) to TcO_4^- . Even as little as $10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ HNO_3 oxidized Tc(V) oxochlorides to TcO_4^- at a significant rate (KG84b). HNO_3 can also oxidize some technetium complexes with organic ligands, e.g. carbonyl halides, to TcO_4^- (LP70). However, hydrolyzed Tc(IV), i.e. $\text{TcO}(\text{OH})_n^{2-n}$, was not oxidized by 0.01-0.10 $\text{mol}\cdot\text{dm}^{-3}$ KNO_3 at pH=1 and 2 in the presence of hydrazine (GK69).

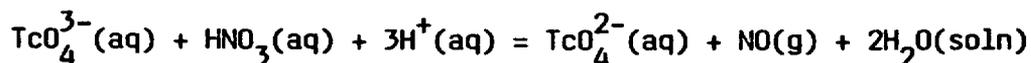
The oxidation of aqueous Pu^{3+} to Pu^{4+} with HClO_4 - HNO_3 mixtures or with HNO_3 has been studied using TcO_4^- as a catalyst (SR81, RS81). Their proposed reaction mechanism involved



and



followed by reoxidation of $\text{TcO}_4^{3-}(\text{aq})$ by HNO_3 (their incorrect reaction stoichiometry):



This TcO_4^{2-} is subsequently reoxidized to TcO_4^- by the HNO_3 . If these reactions are basically correct, then this implies that it might be possible to prepare solid reduced valence technetium nitrates or oxonitrates by adding a mild reducing agent to TcO_4^- - HNO_3 solutions.

Spitsyn et al. (SK83) studied reduction of TcO_4^- in aqueous HNO_3 by using reduction with hydrazine. At HNO_3 concentrations of $< 1.0 \text{ mol}\cdot\text{dm}^{-3}$, hydrazine reduced TcO_4^- with precipitation of Tc(IV) and Tc(V) hydrous oxides (note: there is no other confirmatory evidence for Tc(V) oxide). In $> 8 \text{ mol}\cdot\text{dm}^{-3}$ HNO_3 , hydrazine concentrations of up to $1 \text{ mol}\cdot\text{dm}^{-3}$ did not reduce TcO_4^- . However, at various HNO_3 concentrations, high concentrations of both N_2H_4 and TcO_4^- reacted explosively to form a complex. This complex was isolated in solid form, and identified as $\text{TcO}(\text{NO}_3)_3\cdot\text{H}_2\text{O}$. No details of its identification were provided.

A nitrate complex has also been reported in which TcO_4^- acts as a coordinating anion (M75b, MK79). Liquid extraction of UO_2^{2+} from aqueous acidic TcO_4^- - HNO_3 solutions containing tributylphosphate, TBP, gave evidence for the formation of $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\cdot 2\text{TBP}$. Liquid-liquid extraction of TcO_4^- was studied between solutions of triaurilammonium nitrate ($\text{TAA}\cdot\text{HNO}_3$) in o-xylene and aqueous HNO_3 - LiNO_3 (BD64). Evidence was obtained there for the formation of $(\text{TAAH})_2(\text{NO}_3)(\text{TcO}_4)$ and $(\text{TAAH})_3(\text{NO}_3)_2(\text{TcO}_4)$ in the organic phase.

Linder et al. (LD86) prepared the tert-butyl isocyanide complex ion $[\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6]^+$ in aqueous ethanol. Addition of excess NH_4NO_3 followed by rotary evaporation gave a white solid that they identified as $[\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6]\text{NO}_3$, based on ^1H NMR and cyclic voltammetry measurements.

The polarographic reduction of NH_4TcO_4 has been studied in $1 \text{ mol}\cdot\text{dm}^{-3}$ KNO_3 with and without added KOH (SK65). It was necessary to add a maximum suppressor. Two reduction waves were observed with $E_{1/2} \sim -0.7$ and ~ -1.6 V. In the presence of HNO_3 , the first reduction occurred at -0.6 V. For comparison, the first reduction of TcO_4^- in Cl^- , ClO_4^- , or OH^- occurs in the range -0.52 to -0.63 V, see sect. 9. At least in the HNO_3 solutions, this polarographic study provides no evidence for technetium nitrate complexes.

Solutions of NaNO_2 in H_2SO_4 , HCl , or H_2SO_4 - H_3PO_4 mixtures do not reduce TcO_4^- even with heating (R70). In fact, dilute solutions

of HNO_2 in $1\text{--}4 \text{ mol}\cdot\text{dm}^{-3}$ HCl oxidize Tc(V) oxochlorides to TcO_4^- (KG84c).

The first step of the polarographic reduction of TcO_4^- in NH_4Cl solutions occurs at -0.56 V (MK60), which is in the range reported for TcO_4^- in Cl^- , ClO_4^- , or OH^- solutions (R83). That study (MK60) thus provided no evidence for the formation of ammonia complexes of technetium. The corresponding reductions of NH_4TcO_4 and also its solutions in KOH were reported (SK65), unfortunately, only as a small-scale figure. Unlike most other ionic media in which two reduction waves are observed, reduction of NH_4TcO_4 in aqueous KOH occurs with a single reduction wave at about -0.7 V . The presence of this KOH should have converted all of the NH_4^+ to NH_4OH . Polarographic measurements for the reduction of TcO_4^- in $1 \text{ mol}\cdot\text{dm}^{-3}$ KCl in the presence of $0.43\text{--}3.3 \text{ mol}\cdot\text{dm}^{-3}$ NH_4OH (SK70) give very similar results to the previous study (SK65), and have no maximum in the catalytic current. In contrast, polarograms taken without NH_4OH have a maximum in the catalytic current (SK70). This reduction of TcO_4^- in $0.2 \text{ mol}\cdot\text{dm}^{-3}$ NH_3 solutions has a polarographic limiting current corresponding to a $3e^-$ reduction (D79).

Several studies have been reported for the reduction of TcO_4^- by hydrazine in solutions of aqueous alkali (G56, RP67, MP69, GB77). In three of these studies it was reported that the initial reduction of TcO_4^- is to TcO_4^{2-} , which then reacts with water and disproportionates to TcO_4^- and hydrated TcO_2 (G56, RP67, MP69). Attempts to isolate this TcO_4^{2-} as a barium salt did not give reproducible results (RP67, MP69), but a salt of TcO_4^{2-} has since been prepared electrochemically under anhydrous conditions (see sect. 9). In another study (GB77), however, it was claimed that the initial reduction of TcO_4^- by hydrazine involved $2e^-$ rather than $1e^-$. In HClO_4 solutions, hydrazine ultimately reduces TcO_4^- completely to hydrolyzed forms of Tc(IV) (GK69). No complexes between technetium and hydrazine were suggested in these studies.

Reduction of TcO_4^- by hydrazine in aqueous H_2SO_4 yields Tc(IV) (G56). The corresponding reduction of TcO_4^- with hydrazine in aqueous HCl was reported to yield $\text{Tc}_2\text{Cl}_6^{2-}$ (KG86c). The reduction kinetics (KG86c) followed the rate equation

$$-d[\text{TcO}_4^-]/dt = k [\text{TcO}_4^-][\text{N}_2\text{H}_5^+]^{0.85}[\text{H}^+]^{1.4}$$

To explain this dependence on hydrazine and hydrogen ion concentrations, the authors invoked formation of $\text{N}_2\text{H}_5[\text{TcO}_4]$ ion-pairs in the initial stages of the reduction. In addition, they suggested that TcO_4^- can react with 2H^+ to form TcO_3^+ , and this species is then reduced by hydrazine to HTcO_4^- .

Frlec et. al. (FS67) reacted $\text{N}_2\text{H}_4 \cdot 2\text{HF}$ with TcF_6 in anhydrous HF; they thus prepared yellowish-orange material with the empirical composition $\text{N}_2\text{H}_6[\text{TcF}_6]_2$, and brown $\text{N}_2\text{H}_6[\text{TcF}_6]$. This $\text{N}_2\text{H}_6[\text{TcF}_6]_2$ decomposes to $\text{N}_2\text{H}_6[\text{TcF}_6]$ at about room temperature in the presence of excess fluoride. The magnetic moment of $\text{N}_2\text{H}_6[\text{TcF}_6]$ is 3.79 BM at 300 K, its crystals have a cubic cell with $a = 10.48 \times 10^{-10}$ m, and it is soluble in an excess of HF. IR spectra were also reported. We would expect $\text{N}_2\text{H}_6[\text{TcF}_6]_2$ to react readily with water, with TcF_6^- being converted to TcF_6^{2-} .

Kaden et al. (KL79) prepared a complex TcN_2L_2 which contains molecular dinitrogen, where $\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. It was prepared by reaction of L with $\text{TcCl}_4[\text{PPh}_3]_2$ and sodium amalgam in benzene under dinitrogen. This complex forms yellow crystals with a strong IR absorption band at 2046 cm^{-1} due to N_2 (the $^{14}\text{N}^{15}\text{N}$ complex absorbs at 2014 cm^{-1}). It is "stable" in air for several hours; it is soluble in benzene and toluene; but it is sparingly soluble in ethanol and hexane.

A large number of complexes have been reported in which technetium is coordinated with an organic nitrogen donor ligand (BM82, DL83, MV87). Some of these are described in section 7.

5.2.1 Phosphorus Compounds

Compounds that are formed between technetium and phosphorus were first described in 1982 (RJ82a, RJ82b). Six different solid technetium phosphides were prepared by reaction of technetium with red phosphorus at 1220 K either using tin as a flux or iodine as a mineralizer. Samples prepared with a tin flux were subsequently treated for one day with dilute HCl to dissolve away the tin matrix.

Three of these phosphides were characterized by x-ray diffraction. Tc_3P crystallized in the tetragonal Fe_3P -type structure with $a = (9.568 \pm 0.005) \times 10^{-10}$ and $c = (4.736 \pm 0.003) \times 10^{-10}$ m (RJ82a). TcP_4 crystallized in the orthorhombic ReP_4 -type structure with $a = (6.238 \pm 0.001) \times 10^{-10}$, $b = (9.215 \pm 0.003) \times 10^{-10}$, and $c = (10.837 \pm 0.003) \times 10^{-10}$ m (RJ82a). TcP_3 crystallized in the orthorhombic space group P_{nma} with $a = (15.359 \pm 0.005) \times 10^{-10}$, $b = (3.092 \pm 0.001) \times 10^{-10}$, and $c = (5.142 \pm 0.002) \times 10^{-10}$ m. It is black with a metallic luster and was not attacked by boiling HCl (RJ82b). The valence of Tc is +2 in TcP_4 and +3 in TcP_3 . Three other phases were found but not identified (RJ82a); they have the composition TcP_m , with m approximately 0.7, 1.2, and 2.0. None of these phosphides have thermodynamic data.

A number of solid organotechnetium phosphine, phosphonate, and phosphonium complexes have been prepared and structurally characterized. Three recent reviews tabulated structural data for them (BM82, DL83, MV87), and Deutsch et al. tabulated the methods of synthesis (DL83).

Electrolysis of aqueous TcO_4^- in the presence of phosphate, pyrophosphate, and tripolyphosphate produced a variety of complexes of technetium with these ions. Electrochemical evidence for complex formation have been summarized (MK60, SR63, TZ63, SM78, RC78, M83). Depending on which oxyphosphate(V) ligand was used at what pH value, reduction can occur to form Tc(IV), Tc(III), or, in some cases, Tc(II) aqueous complexes. Some of these complexes may be dimeric or polymeric, some may be mixed valence technetium complexes, and some may be hydroxy-oxophosphorus(V) complexes. Spectroscopic data confirm the presence of complexes of Tc(III) and Tc(IV) in phosphate solutions (PL82). They are described in section 5.2.2. No solid inorganic oxyphosphorus salts have been characterized for technetium.

5.3 Other Pnictide Compounds and Complexes

In 1966 Hulliger (H66) reported preparation of the non-metallic arsenide Tc_3As_7 , along with a number of other compounds of this structure type not containing technetium. Hulliger stated that these phases "...were prepared either by sintering the components in the form of pressed powder pellets or by melting, quenching and subsequent annealing at temperatures

between 450° and 900°C". The phase of interest formed peritectically. Unfortunately, no specific details were given for the preparation or characterization of Tc_3As_7 .

Jeitschko and Dietrich (JD85) investigated the reaction of technetium with arsenic in a sealed silica tube with a small amount of I_2 added to promote crystal growth. Samples with initial Tc:As atomic ratios of 1:3 and 1:9 that were annealed at 1223 K for two weeks and then quenched produced Tc_2As_3 along with excess arsenic. Another sample with a Tc:As starting ratio of 1:2 gave a different and unidentified phase.

A single crystal x-ray structural determination (JD85) indicated that Tc_2As_3 crystallized in the triclinic space group $P\bar{1}$ with $a = (6.574 \pm 0.001) \times 10^{-10}$, $b = (6.632 \pm 0.001) \times 10^{-10}$, $c = (8.023 \pm 0.002) \times 10^{-10}$ m, $\alpha = 95.69 \pm 0.01^\circ$, $\beta = 102.03 \pm 0.01^\circ$, $\gamma = 104.31 \pm 0.02^\circ$, and $Z = 4$. Each of the four nonequivalent Tc atoms has six neighboring As atoms that form very distorted octahedra.

There seems to be a lack of data for the technetium-antimony and technetium-bismuth systems. However, an antimony sulphide colloid containing technetium is sometimes used in nuclear medicine for imaging of liver, spleen, and bone marrow (GP65, PV77). These colloids are generally prepared by mixing antimony trisulphide with potassium hydrogen tartrate in aqueous HCl, with polyvinyl pyrrolidone added as a stabilizer. A saline solution of TcO_4^- from a Mo/Tc generator is then added to the mixture, and the resulting solution heated in a boiling water bath to produce the desired product. Binding of technetium to this colloid is virtually complete, but nothing is known of the chemical state of technetium.

Several complexes have been reported in which technetium is directly coordinated with an arsenic atom. All of these complexes contain organoarsenic ligands: diarsine (diars = o-phenylenebis(dimethylarsine)), triphenylarsine Ph_3As , or diphenylarsine Ph_2As . Technetium salts containing the Ph_4As^+ cation are also known, but since they contain a non-coordinating arsenic, they are not considered in this section.

The first complexes with arsenic to be reported contained diarsine (FN59). Fergusson and Nyholm reported that if K_2TcCl_6 was dissolved in

aqueous alcoholic HCl that contained excess diarsine, and then the solution was refluxed, orange colored $[\text{Tc(III)(diars)}_2\text{Cl}_2]\text{Cl}$ formed. If this compound was then refluxed with LiBr in ethanol, it was converted into red $[\text{Tc(III)(diars)}_2\text{Br}_2]\text{Br}$. If this, in turn, was refluxed with LiI in ethanol, $[\text{Tc(III)(diars)}_2\text{I}_2]\text{I}$ was produced. Addition of excess I_2 then produced deep red to black $[\text{Tc(III)(diars)}_2\text{I}_2]\text{I}_3$. Refluxing $[\text{Tc(III)(diars)}_2\text{I}_2]\text{I}$ in alcohol, especially in the presence of SO_2 , produced brown $[\text{Tc(II)(diars)}_2\text{I}_2]$; it could be reoxidized to the parent species by I_2 .

They (FN59) found that $[\text{Tc(III)(diars)}_2\text{X}_2]\text{X}$ with $\text{X} = \text{Cl}$ or Br , $[\text{Tc(III)(diars)}_2\text{I}_2]\text{I}_3$, and $[\text{Tc(II)(diars)}_2\text{I}_2]$ all had magnetic moments around 2.7 to 3.4 BM. The electrical conductances of the Tc(III) complexes in nitromethane at 298 K were measured, and they indicated that these complexes dissociate as 1-1 electrolytes. In contrast, the Tc(II) complex is non-conducting in nitrobenzene or nitromethane.

In 1960, Fergusson and Nyholm (FN60) reported that $[\text{Tc(III)(diars)}_2\text{Cl}_2]\text{Cl}$ could be oxidized by Cl_2 to form brown $[\text{Tc(V)(diars)}_2\text{Cl}_4]\text{ClO}_4$, but that Ce^{4+} was not effective for this oxidation. Reaction of the perchlorate salt with TiCl_3 reduced it back to the Tc(III) complex. The $[\text{Tc(III)(diars)}_2\text{Cl}_2]\text{Cl}$ could be reduced to yellow $[\text{Tc(II)(diars)}_2\text{Cl}_2]$ by use of H_3PO_2 , and this could then be oxidized with Cl_2 to the parent complex. They also prepared $[\text{Tc(II)(diars)}_2\text{X}_2]$, where $\text{X} = \text{Br}$ or I . IR measurements were reported (LN65) for the Tc-Cl stretching frequencies of $[\text{Tc(II)(diars)}_2\text{Cl}_2]$, hydrated $[\text{Tc(III)(diars)}_2\text{Cl}_2]\text{Cl}$, and $[\text{Tc(III)(diars)}_2\text{Cl}_2]\text{ClO}_4$. The redox potentials for the $[\text{Tc(III)(diars)}_2\text{X}_2]^+ / [\text{Tc(II)(diars)}_2\text{X}_2]$ couple, with $\text{X} = \text{Cl}$, Br , or I were found to be reversible in dimethylformamide containing the corresponding tetraethylammonium perchlorate or tetrabutylammonium bromide salts (H80, HH81). A further reduction, possibly to a Tc(I) complex, was observed but it was irreversible.

Direct formation of $[\text{Tc(III)(diars)}_2\text{Cl}_2]^+$ and $[\text{Tc(III)(diars)}_2\text{Br}_2]^+$ solutions has been reported from reduction of TcO_4^- by HCl or HBr in aqueous ethanol containing diars (NL87). They also reduced $[\text{Tc(III)(diars)}_2\text{Cl}_2]^+$ to $[\text{Tc(II)(diars)}_2\text{Cl}_2]$ by using reduction by NaBH_4 at $\text{pH} = 5$, or with reduction by 2-mercaptoethanol or ascorbic acid

at pH = 4-5. Similarly, $[\text{Tc(III)(diars)}_2\text{Br}_2]^+$ was reduced to $[\text{Tc(II)(diars)}_2\text{Br}_2]$ by 2-mercaptoethanol at pH = 6, or by reduction with ascorbic acid at pH = 4 (NL87).

Crystal structural data have been reported for four technetium diarsine complexes. Single crystals of orange $[\text{Tc(diars)}_2\text{Cl}_2]\text{ClO}_4$ were grown from an ethanol solution of $[\text{Tc(diars)}_2\text{Cl}_2]^+$ containing 10^{-4} mol·dm⁻³ HClO₄ (GW80). It crystallized in the monoclinic space group C2 with $a = (13.001 \pm 0.010) \times 10^{-10}$, $b = (10.409 \pm 0.003) \times 10^{-10}$, $c = (11.796 \pm 0.008) \times 10^{-10}$ m, $\beta = 114.49 \pm 0.15^\circ$, and $Z = 2$. The $[\text{Tc(diars)}_2\text{Cl}_2]^+$ cation has a trans structure.

Oxidation of $[\text{Tc(diars)}_2\text{Cl}_2]\text{ClO}_4$ with Cl₂ in an ethanol solution yielded dark-brown $[\text{Tc(diars)}_2\text{Cl}_4]\text{ClO}_4$ (GW80). Ligand exchange with PF₆⁻ in nitromethane then gave dark-brown $[\text{Tc(diars)}_2\text{Cl}_4]\text{PF}_6$. The crystals of the latter compound were orthorhombic with space group Fddd and $a = (13.821 \pm 0.004) \times 10^{-10}$, $b = (21.159 \pm 0.008) \times 10^{-10}$, $c = (21.227 \pm 0.018) \times 10^{-10}$ m, and $Z = 8$. The $[\text{Tc(diars)}_2\text{Cl}_4]^+$ cation has D_{2d} dodecahedral coordination with technetium in the unusual eight-coordinated state.

The dark-red salt $[\text{Tc(diars)}_2\text{Cl}_2]\text{Cl}$ crystallized in the monoclinic space group P2₁/c with $a = (9.354 \pm 0.005) \times 10^{-10}$, $b = (9.662 \pm 0.002) \times 10^{-10}$, $c = (15.341 \pm 0.004) \times 10^{-10}$ m, $\beta = 98.75 \pm 0.06^\circ$, and $Z = 2$ (EW80). They also studied yellow-orange $[\text{Tc(diars)}_2\text{Cl}_2]\text{ClO}_4$, which crystallized in the monoclinic space group C2 with $a = (13.001 \pm 0.010) \times 10^{-10}$, $b = (10.409 \pm 0.003) \times 10^{-10}$, $c = (11.796 \pm 0.008) \times 10^{-10}$ m, $\beta = 114.50 \pm 0.15^\circ$, and $Z = 2$. Perchlorate ions in this salt are rotationally disordered. In both cases, $[\text{Tc(diars)}_2\text{Cl}_2]^+$ has trans chloride ligands and four As atoms coordinated to the technetium.

Fergusson and Hickford (FH66) prepared a compound which they formulated as $\text{TcCl}_4(\text{Ph}_3\text{As})_2$ by reaction of TcCl_4 with Ph_3As in ethanol. This complex is brown, and it has a magnetic moment of 3.62 BM. The electronic spectrum of this complex was also reported. Hieber and Opavsky (HO68b) reacted technetium carbonyl chloride $\text{Tc(CO)}_5\text{Cl}$ with (presumably) $\text{Ph}_2\text{AsAsPh}_2$ in benzene to produce $[\text{Cl(CO)}_3\text{TcAsPh}_2]_2$. It was only

characterized by elemental analysis for Tc, C, and H. They similarly claimed preparation of $[\text{Tc}(\text{CO})_3(\text{AsPh}_3)_2\text{Cl}]$ (HL65).

Hieber et al. (HL65) reported preparing an organostibine complex $[\text{Tc}(\text{CO})_3(\text{SbPh}_3)_2\text{Cl}]$. It was partially characterized by C and H analyses. They prepared it by reaction of $\text{Tc}(\text{CO})_5\text{Cl}$ with Ph_3Sb in an ethanol-benzene mixture at 323-343 K.

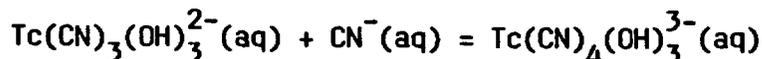
No thermodynamic data are available for these technetium organoarsenic and organostibine complexes. However, since they only form in the presence of these organopnictides, they will not form under normal environmental conditions.

No inorganic or organic bismuth complexes of technetium seem to have been reported.

10. Other Technetium Compounds

10.2 Pseudohalogen and Oxo-pseudohalogen Complexes

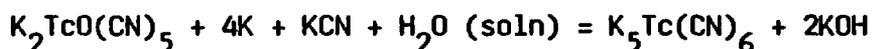
In 1961 Herr and Schwochau (HS61) reported preparation of " $\text{Tl}_3[\text{Tc}(\text{OH})_3(\text{CN})_4]$ " which should contain Tc(IV). More details were given the following year (SH62a). This salt was prepared by dissolution of hydrated $\text{TcO}_2(\text{s})$ in aqueous alkaline cyanide solutions. Addition of Tl^+ salts yielded yellow-brown " $\text{Tl}_3[\text{Tc}(\text{OH})_3(\text{CN})_4]$ " or " $\text{Tl}_3[\text{TcO}(\text{OH})(\text{CN})_4]$ ", as deduced from elemental analysis. This formulation was supported by electrical conductivity, I.R., visible, and U.V. spectra (SH62a). A study of the formation of the corresponding aqueous complex as a function of pH indicated that no cyanide complex forms below pH~5-6, and cyanide complex formation is complete by pH = 9. Measurement of the light absorption (extinction coefficient) as a function of concentration gave information about the equilibrium



for which they determined $K=(1.3\pm 0.6)\times 10^8 \text{ mol}^{-1}\cdot\text{dm}^3$ (presumably at 303 K) for ionic strengths around $10^{-5} \text{ mol}\cdot\text{dm}^{-3}$.

Trop et al. (TJ80) also reacted hydrated TcO_2 with KCN, and showed the product was actually $\text{K}_2\text{TcO}(\text{CN})_5 \cdot 4\text{H}_2\text{O}$ and not a $\text{Tc}(\text{CN})_4(\text{OH})_3^{3-}$ salt, using IR and Raman spectroscopy. Reaction of $(\text{NH}_4)_2\text{TcI}_6$ with KCN in refluxing aqueous methanol in a nitrogen atmosphere gave yellow-orange $\text{K}_4\text{Tc}(\text{CN})_7 \cdot 2\text{H}_2\text{O}$. Its aqueous solutions are air-sensitive and decompose to pale greenish-yellow $\text{K}_2\text{TcO}(\text{CN})_5 \cdot 4\text{H}_2\text{O}$. This cyanide salt can be further hydrolyzed in water to form lemon yellow potassium trans-dioxotetracyanotechnetate(V), $\text{K}_3\text{TcO}_2(\text{CN})_4$. The $\text{TcO}_2(\text{CN})_4^{3-}$ complex has since been studied by ^{99}Tc NMR (FL82). These results suggest that Schwochau and co-workers (HS61, SH62a) actually had studied the Tc(V) complex $\text{TcO}(\text{CN})_5^{2-}$ rather than the Tc(IV) complex $\text{Tc}(\text{CN})_4(\text{OH})_3^{3-}$. Similarly, a claim by Colton for preparation of $\text{Tc}(\text{CN})_6^{4-}$ salts by reaction of TcI_6^{2-} with CN^- in methanol (cited in the Gmelin Handbook (dAB83)) is apparently incorrect, since only $\text{K}_4\text{Tc}(\text{CN})_7 \cdot 2\text{H}_2\text{O}$ has been isolated under these conditions (TJ80).

Preparation of a reduced valence Tc(I) complex was also reported by Schwochau and Herr (SH62b), by reaction of TcO_4^- or " $\text{Tc}(\text{CN})_4(\text{OH})_3^{3-}$ " with potassium amalgam in the presence of KCN. However, as noted above, their " $\text{Tc}(\text{CN})_4(\text{OH})_3^{3-}$ " was probably $\text{TcO}(\text{CN})_5^{2-}$. Thus, the formation from this latter reagent should be given by



$\text{K}_5\text{Tc}(\text{CN})_6$ is olive-green, it forms cubic crystals with $a = (12.106 \pm 0.001) \times 10^{-10}$ m, and it is isostructural with $\text{K}_5\text{Mn}(\text{CN})_6$ and $\text{K}_5\text{Re}(\text{CN})_6$. Its aqueous solutions are very air-sensitive. Both the potassium and thallium salts of $\text{Tc}(\text{CN})_6^{5-}$ have low solubilities in water.

Two studies yield polarographic data for the reduction of $\text{TcO}_4^-(\text{aq})$ in $0.1 \text{ mol} \cdot \text{dm}^{-3}$ KCN (CD60) and in $0.1 \text{ mol} \cdot \text{dm}^{-3}$ KOH- $0.5 \text{ mol} \cdot \text{dm}^{-3}$ KCN (M64). Colton et al. (CD60) reported a $3e^-$ reduction occurred at -0.57 V, and Münze (M64) a $3e^-$ reduction also. Russell and Cash (RC78) found the reduction occurred at -0.55 V at $\text{pH}=13.0$ by anodic-sweep pulse polarography. The number of electrons involved was non-integral, and the reduction wave was irreversible. No useful thermodynamic data can be

derived. Results from microcoulometry (M68b) indicate 3-4e⁻ reductions of TcO₄⁻ can occur in 0.1 mol·kg⁻¹ KOH-0.5 mol·kg⁻¹ KCN, depending on the applied potential.

Al-Kayssi et al. (A-KM62) found that reduction of TcO₄⁻ in aqueous HCl by bismuth amalgam or mercury in the presence of potassium ferrocyanide yields an anionic blue complex; in contrast, for the corresponding reduction with SnCl₂, a yellowish-brown complex is obtained. The stoichiometry of these complexes is unknown.

Crouthamel (C57) claimed that TcO₄⁻ in 3.5-4.0 mol·dm⁻³ aqueous H₂SO₄ was reduced by excess potassium thiocyanate to form a bright red Tc(V) complex, and this reaction can be used for quantitative analysis for technetium, but the stoichiometry of the complex was not determined. Partial formation of a yellow Tc(IV) complex was also reported. In aqueous alkali at pH=13.0-13.2 in the presence of thiocyanate, electrolytic reduction of TcO₄⁻ at -0.61 to -0.54 V forms an unidentified Tc(IV) complex (RC78). This reduction, and the corresponding one for Tc(NCS)₆²⁻ in aqueous acetonitrile (TD79), are irreversible. Reduction of TcO₄⁻ in aqueous alkaline KSCN was also briefly described by Münze (M64). Results from microcoulometry (M68b) indicate 2-5e⁻ reductions of TcO₄⁻ can occur in 0.1 mol·dm⁻³ KOH - 0.5 mol·kg⁻¹ KSCN, depending on the applied potential.

Grases et al. (GF87) studied chemical reduction of TcO₄⁻ in 0.1-3.0 mol·dm⁻³ aqueous HCl in the presence of KSCN. Reduction with SnCl₂ followed by liquid extraction gave yellow and orange Tc(III) complexes, and a red Tc(IV) complex. They may contain different numbers of SCN⁻-groups, and possibly Cl⁻.

Various studies have been reported in which solid complexes of technetium with SCN⁻ have been prepared, and they indicate that bonding in these complexes is through the nitrogens, so these complexes are actually isothiocyanates. Schwochau and Peiper (SP68) reported preparation of a "Tc(V)" complex by reaction of hydrated TcO₂ or reduction of TcO₄⁻ in acidic thiocyanate solutions. They reported the preparation of blackish-violet salts with (CH₃)₄N⁺ and Tl⁺. One of these salts,

"[(CH₃)₄N][Tc(NCS)₆]", was characterized by IR spectra and found to contain Tc-N bonds but not Tc-O bonds. A powder pattern x-ray study of this salt (HS73) indicated a rhombohedral unit cell with $a = 8.84 \times 10^{-10}$ m and $\alpha = 82.9^\circ$.

Schwochau et al. (SA73) further investigated the purported Tc(V)-NCS complex and its reduction product. Their elemental analyses indicated the two salts were (air-sensitive) yellow "[[(CH₃)₄N]₂[Tc(NCS)₆]" and violet "[[(CH₃)₄N][Tc(NCS)₆]." Absorption, UV, and IR spectra were reported, as were molar electrical conductances for their solutions in acetonitrile. These conductance values indicated that (CH₃)₄N⁺ salts behave like 2-1 and 1-1 electrolytes, respectively, in that solvent.

Reinvestigation of technetium isothiocyanato solutions and salts by Trop et al. (TD80b) indicated that Schwochau et al. (SP68, SA73) may have been in error in assigning technetium valences of V and IV to the violet and yellow salts, respectively. Trop et al. (TD80b) prepared purple salts with the stoichiometry (NH₄)₂[Tc(NCS)₆] and (Ph₄As)₂[Tc(NCS)₆] which contain Tc(IV), and yellow to yellow-orange air-sensitive [(n-C₄H₉)₄N]₃[Tc(NCS)₆] and (Ph₄As)₃[Tc(NCS)₆] which contain Tc(III). Both (NH₄)₂TcBr₆ and NH₄TcO₄ could be reacted with NH₄SCN in methanol to prepare them. A detailed single crystal x-ray structure determination for [(n-C₄H₉)₄N]₃[Tc(NCS)₆] showed it was cubic, with $a = (24.444 \pm 0.006) \times 10^{-10}$ m, $Z=8$, and space group $P_{a3} \cdot H_2O_2$ oxidizes Tc(NCS)₆³⁻ solutions to TcO₄⁻ and SCN⁻. Addition of NO(g) to Tc(NCS)₆³⁻ solutions in dichloromethane yields Tc(NCS)₆²⁻ solutions. The Tc(NCS)₆²⁻/Tc(NCS)₆³⁻ redox couple in acetonitrile is 1e⁻ and reversible at -0.06 V. Since the purple species was obtained upon oxidation of the yellow species, this confirmed that the violet-to-purple solutions and solid complexes contained Tc(IV). Addition of Ce(IV) or thiocyanogen (SCN)₂ to non-aqueous solutions of Tc(NCS)₆³⁻ produced Tc(NCS)₆²⁻ rapidly.

March and Grases (MG88) reported that TcO₄⁻(aq) was not reduced by aqueous 0.3 to 2.0 mol·dm⁻³ HCl in the presence of thiocyanate. When enough SnCl₂ was added to reduce the Tc(VII) to Tc(IV), the solution turned red. If even more SnCl₂ was added, then the solution turned

yellow. Liquid-liquid extraction and absorption spectra measurements indicated that the yellow and red complexes were $\text{Tc}(\text{NCS})_6^{3-}$ and $\text{Tc}(\text{NCS})_6^{2-}$.

Davison et al. (DJ81b) have since prepared a bonafide Tc(V) complex with isothiocyanate, but is is an oxopentakis(isothiocyanato)technetate(V) complex. They prepared it by using ligand substitution of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{TcOCl}_4$ with NH_4SCN in methanol. Subsequent addition of $\text{Ph}_4\text{AsCl}\cdot\text{H}_2\text{O}$ yielded fine bright red crystals of $(\text{Ph}_4\text{As})_2\text{TcO}(\text{NCS})_5$. Elemental analysis, optical spectroscopy in acetonitrile, and IR spectra in solid KBr were used to partially characterize this salt.

Addition of excess KSCN to solutions of $\text{TcO}(\text{NCS})_5^{2-}$ in acetonitrile gave complete reduction to a $\text{Tc}(\text{NCS})_6^{2-}$ and $\text{Tc}(\text{NCS})_6^{3-}$ mixture within 24 hours; small amounts of self-ionization of $\text{TcO}(\text{NCS})_5^{2-}$ yielded enough free SCN^- to produce slow autoreduction of this complex even in the absence of excess SCN^- . Addition of AgNO_3 to $\text{TcO}(\text{NCS})_5^{2-}$ solutions produced a $\text{Ag}_2\text{TcO}(\text{NCS})_5\text{-AgSCN}$ mixture, with partial reduction to $\text{Tc}(\text{NCS})_6^{2-}$ also occurring (DJ81b).

Spitsyn et al. (SG71) found that when NH_4SCN was added to aged solutions of TcOCl_5^{2-} in $3 \text{ mol}\cdot\text{dm}^{-3}$ HCl, a raspberry-red complex was produced that could readily be extracted with diethylether or butyl acetate. They assigned it the formula $[\text{TcO}(\text{OH})(\text{CNS})_4]^{2-}$, but it may well have been identical to Davison et al.'s (DJ81b) $[\text{TcO}(\text{NCS})_5]^{2-}$. Dissolution of $\text{K}_2[\text{TcOCl}_5]$ in concentrated HCl in the presence of SCN^- was reported by them to yield an unidentified complex with "the color of strong tea".

Two nitrosylisothiocyanates are described in the next section.

10.3 Nitrosyl Complexes

In 1963 Eakins et al. (EH63a) reported the preparation of a pink crystalline complex which they formulated as $[\text{Tc}(\text{NH}_2\text{OH})_2(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_2$. This empirical formula was based on a partial chemical analysis and by

determining the number of equivalents of ceric sulphate required to oxidize it to form TcO_4^- , and the presence of one molecule of water was assumed to give the technetium atom 6-coordination. This "pink complex" was prepared by reacting aqueous $(\text{NH}_4)_2\text{TcCl}_6$ with hydroxylamine hydrochloride $\text{NH}_2\text{OH}\cdot\text{HCl}$ followed by evaporation to dryness; the solution was then extracted several times with diethylether, and subsequently aqueous ammonia was added until $\text{pH}=7$. The result was a mixture, from which the above complex was isolated and purified by several dissolutions in water followed by precipitations with absolute ethanol.

A later detailed study by Armstrong and Taube (AT76) leaves no doubt that the complex prepared by Eakins et al. (EH63a) was actually the complex $\text{trans-}[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{H}_2\text{O})]\text{Cl}_2$. In most nitrosyl complexes, the nitrosyl group is assigned a +1 charge, so they assumed their complex contained Tc(I). They cited an as of then unpublished study by Radonovich and Hoard in which x-ray diffraction was used to determine the structure of this complex. Armstrong and Taube (AT76) followed Eakins et al.'s (EH63a) method of preparation, except that they purified the complex by cation-exchange using $1 \text{ mol}\cdot\text{dm}^{-3}$ HCl as the eluting agent. The complex could be converted to a methane sulfonate solution by elution with methanesulfonic acid; addition of solid KBr or concentrated HBF_4 solutions then gave precipitates of the corresponding Br^- and BF_4^- salts. The trifluoroacetate salt was prepared by ion-exchange with the chloride salt. A phenanthroline complex was also briefly mentioned (AT76), and it was formulated as $[\text{Tc}(1,10\text{-phen})_2(\text{NH}_3)(\text{NO})]^{2+}$.

The results from potentiometric pH titration indicate that the water in $\text{trans-}[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{H}_2\text{O})]^{2+}$ behaves as an acid with $\text{pK}_a=7.3$ at $I = 0.01 \text{ mol}\cdot\text{dm}^{-3}$ and 298 K (AT76). At pH values above the end-point, solutions of the "pink complex" slowly decompose in air. Solutions of "pink complex" in $2 \text{ mol}\cdot\text{dm}^{-3}$ HClO_4 or $\text{CF}_3\text{SO}_3\text{H}$, or in dilute HCl or HBr, appear to be stable, but in $2 \text{ mol}\cdot\text{dm}^{-3}$ HCl or HBr this complex undergoes slow decomposition to form a green solid. The solubility of the pink chloride complex in water is $>0.03 \text{ mol}\cdot\text{dm}^{-3}$.

Oxidation of the "pink complex" by electrochemical or chemical methods (Ce^{4+} or MnO_4^-) in acidic solutions yields the green complex of

"Tc(II)", $\text{trans-}[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{H}_2\text{O})]\text{Cl}_3$ (AT76). Results from cyclic voltammetry in $3.0 \text{ mol}\cdot\text{dm}^{-3}$ trifluoromethanesulfonate indicate that water in the aqueous complex $[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{H}_2\text{O})]^{3+}$ behaves as an acid with $\text{pK}_a \sim 2.0$. Solutions of the "pink complex" stored in $2 \text{ mol}\cdot\text{dm}^{-3}$ HCl slowly form a solid containing impure $(\text{NH}_4)_2[\text{Tc}(\text{NO})\text{Cl}_5]$. The $[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{H}_2\text{O})]^{3+}/[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{H}_2\text{O})]^{2+}$ redox couple in aqueous $3 \text{ mol}\cdot\text{dm}^{-3}$ trifluoromethanesulfonate solution is reversible at 0.80 V for $\text{pH} \leq 2$, but it is irreversible above $\text{pH}=2$ (AT76). Yang et al. (YH82) have reported ESR spectra for several of the nitrosyl chloride salts described above.

Radonovich and Hoard (RH84) have published the results of their crystal structural determination for $\text{trans-}[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{OH}_2)]\text{Cl}_2$. It crystallized in the monoclinic space group $\text{P}2_1/\text{m}$ with $a = (6.858 \pm 0.002) \times 10^{-10}$, $b = (10.579 \pm 0.003) \times 10^{-10}$, $c = (6.646 \pm 0.002) \times 10^{-10}$ m, $\beta = 94.01 \pm 0.02^\circ$, and $Z = 2$. The Tc-NO linkage is nearly linear with a $(1.716 \pm 0.004) \times 10^{-10}$ m bond distance. They found that the charge on the nitrosyl group was about -0.5, so this complex contains Tc with a valence of about +2.5.

Holloway and Selig (HS68) investigated reactions of nitric oxide, nitrosyl fluoride, and nitryl fluoride with solid TcF_6 ; the reactions produced $(\text{NO})\text{TcF}_6$, $(\text{NO})_2\text{TcF}_8$, and $(\text{NO}_2)\text{TcF}_7$ as indicated by elemental analyses, IR spectra, and magnetic susceptibilities. They are ionic compounds, and they are hydrolyzed by water to form aqueous TcF_6^{2-} .

Orvig (O81; also see JD82) dissolved freshly precipitated hydrated TcO_2 in $4 \text{ mol}\cdot\text{dm}^{-3}$ HBr under a N_2 atmosphere at 348 K; after purging the solution with $\text{NO}(\text{g})$ for about five minutes, the solution turned blood red. The solution was evaporated and then aqueous $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ added; a bright red solid precipitated immediately. Crystals were grown from acetone and acetonitrile/ether solutions. The empirical formula of this complex is $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Tc}(\text{NO})\text{Br}_4]$ based on elemental analysis, and optical and IR spectra. It behaves like a 1-1 electrolyte in acetonitrile, and it has a magnetic moment of 1.8-1.9 BM. By a slight modification of this technique, red $[(\text{CH}_3)_4\text{N}][\text{Tc}(\text{NO})\text{Br}_4]$ could be

prepared. It is water soluble and a good starting material for synthesis of other nitrosyl technetium complexes.

When $[(\text{CH}_3)_4\text{N}][\text{Tc}(\text{NO})\text{Br}_4]$ and NH_4NCS were dissolved in methanol and refluxed, the solution turned inky blue (081). To this solution $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ was added; after about 12 hours blue needles had deposited. They had the empirical composition $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Tc}(\text{NO})(\text{NCS})_5]$ based on chemical analysis, and IR and optical spectra. This compound had a magnetic moment of 1.5 BM and behaved like a 1-2 electrolyte in acetonitrile. If a solution of $[(\text{CH}_3)_4\text{N}][\text{Tc}(\text{NO})\text{Br}_4]$ with NH_4NCS was purged with nitrogen and hydrazine hydrate added, then a rusty red-brown color immediately formed, from which rust colored $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{Tc}(\text{NO})(\text{NCS})_5]\cdot\text{H}_2\text{O}$ could be isolated. It behaves as a 1-3 electrolyte in acetonitrile, and the $[\text{Tc}(\text{NO})(\text{NCS})_5]^{2-}/[\text{Tc}(\text{NO})(\text{NCS})_5]^{3-}$ redox couple is reversible in acetonitrile. Solid $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{Tc}(\text{NO})(\text{NCS})_5]\cdot\text{H}_2\text{O}$ is air stable, but its solutions turn blue slowly in the presence of air. It should be noted that in the absence of HBr, NO(g) gas in deaerated dichloromethane oxidizes $\text{Tc}(\text{NCS})_6^{3-}$ to $\text{Tc}(\text{NCS})_6^{2-}$ without nitrosyl formation (TD80b).

When $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Tc}(\text{NO})\text{Br}_4]$ was dissolved in concentrated HCl and heated for several hours at 323 K, the solution color changed from red to yellow (081). Upon cooling and concentrating the solution under vacuo, poorly formed yellow plates were separated. Recrystallization from acetonitrile/ether gave bright yellow-green plates of material with the empirical composition $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Tc}(\text{NO})\text{Cl}_4]\cdot\text{H}_2\text{O}\cdot\frac{3}{4}(n\text{-C}_4\text{H}_9\text{OH})$. Its IR and optical spectra were studied, and it had a magnetic moment of 1.9 BM (081).

Also, $[(\text{CH}_3)_4\text{N}][\text{Tc}(\text{NO})\text{Br}_4]$ was dissolved in excess pyridine and refluxed for 24 h; cooling of the solution resulted in precipitation of $[(\text{CH}_3)_4\text{N}]\text{Br}$ (081). The remaining solution was evaporated under reduced pressure to yield a red residue. Extraction of this residue with acetone gave a red solution, from which deep red $\text{Tc}(\text{NO})\text{Br}_2\text{py}_3$ was isolated by slow evaporation of solvent. This compound is diamagnetic and it is non-conducting in acetonitrile.

The original preparation of $\text{Tc}(\text{NO})\text{Br}_4^-$ was attributed to Kuzina et al. (K072) in several review articles (DL83, CF82), but that report was concerned with amine chloride complexes of technetium, rather than nitrosyl bromide complexes. EPR spectra have been reported for frozen solutions of $[\text{Tc}(\text{NO})(\text{NCS})_5]^{2-}$, $[\text{Tc}(\text{NO})\text{Cl}_5]^{2-}$, $[\text{Tc}(\text{NO})\text{Br}_4]^-$, and $[\text{Tc}(\text{NO})\text{I}_4]^-$ (AK88).

Linder et al. (LD86) prepared the tert-butyl isocyanide complex $[\text{Tc}(\text{NO})(\text{CNC}(\text{CH}_3)_3)_5](\text{PF}_6)_2$ by reaction of $\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6^+$ with HNO_3 or NOPF_6 in glacial acetic acid. It crystallized as yellow needles. It was partially characterized by elemental analysis, IR and ^1H NMR spectroscopy, and mass spectrometry. Reaction of $[\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$ with $\text{NO}(\text{g})$ in CH_2Cl_2 with N_2 and dry air gave only very low yields of $[\text{Tc}(\text{NO})(\text{CNC}(\text{CH}_3)_3)_5](\text{PF}_6)_2$. They also prepared $\text{Tc}(\text{NO})\text{Br}_2(\text{CNC}(\text{CH}_3)_3)_3$ by reaction of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Tc}(\text{NO})\text{Br}_4]$ with tert-butyl isocyanide in deoxygenated methanol. Purple crystals of $\text{Tc}(\text{NO})\text{Br}_2(\text{CNC}(\text{CH}_3)_3)_3$ formed; they have the space group $\text{P2}_1\text{cn}$ with $a = (10.985 \pm 0.002) \times 10^{-10}$, $b = (14.250 \pm 0.002) \times 10^{-10}$, $c = (14.677 \pm 0.002) \times 10^{-10}$ m, and $Z=4$.

Other organic technetium nitrosyl complexes have been prepared and then structurally characterized by x-ray diffraction. Brown et al. have prepared the methanol derivative $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Tc}(\text{NO})\text{Cl}_4(\text{CH}_3\text{OH})]$ (BN87) and the pentane-2,4-dionato derivative $[\text{Ph}_4\text{As}][\text{Tc}(\text{NO})\text{Cl}_3(\text{C}_5\text{H}_7\text{O}_2)]$ (BN88a). The first of these compounds crystallized in the monoclinic space group $\text{P2}_1/\text{n}$ with $a = (11.350 \pm 0.010) \times 10^{-10}$, $b = (11.450 \pm 0.005) \times 10^{-10}$, $c = (22.154 \pm 0.010) \times 10^{-10}$ m, $\beta = 91.5 \pm 0.2^\circ$, with $Z = 4$. The second one crystallized in the triclinic space group $\text{P}\bar{1}$ with $a = (10.261 \pm 0.004) \times 10^{-10}$, $b = (11.261 \pm 0.010) \times 10^{-10}$, $c = (13.686 \pm 0.010) \times 10^{-10}$ m, $\alpha = 101.7 \pm 0.5^\circ$, $\beta = 91.9 \pm 0.5^\circ$, $\gamma = 97.3 \pm 0.5^\circ$, and $Z = 2$.

Brown et al. (BN88b) subsequently reported preparation of a trichloronitrosyl(acetylacetonato)technetium(II) salt. It was prepared by reaction of acetylacetone with $[\text{Tc}(\text{NO})\text{Cl}_4\text{X}]^{n-}$ ($\text{X}=\text{Cl}^-$ or H_2O) in aqueous HCl , followed by extraction with CH_2Cl_2 . Evaporation of the residue followed by its dissolution in methanol-water gave a red solution. Addition of Ph_4AsCl followed by evaporation yielded red crystals of

[Ph₄As][Tc(NO)(acac)Cl₃]. It crystallized in the triclinic space group P1 with $a = (10.261 \pm 0.004) \times 10^{-10}$, $b = (11.261 \pm 0.010) \times 10^{-10}$, $c = (13.686 \pm 0.010) \times 10^{-10}$ m, $\alpha = 107.5 \pm 0.5^\circ$, $\beta = 91.9 \pm 0.5^\circ$, $\gamma = 97.3 \pm 0.5^\circ$, and $Z=2$. The

trichloronitrosyl(acetylacetonato)technetium(II) anion has a distorted octahedral geometry with two trans-chlorides, and the other chloride and the nitrosyl occupy the other two positions randomly. This compound was partially characterized by elemental analysis, mass spectrometry, IR, and ESR.

No thermodynamic data are available for nitrosyl complexes of technetium.

10.4 Tin Complexes

There have been no reports of formation of intermetallic compounds between technetium and tin. Alekseyevskiy et al. (AB75) reported unit cell parameters for Tc-Sn (single phase?) hexagonal alloys: for Tc + 22 % Sn, $a = 2.741 \times 10^{-10}$ and $c = 4.406 \times 10^{-10}$ m, and for Tc + 37 % Sn, $a = 2.736 \times 10^{-10}$ and $c = 4.396 \times 10^{-10}$ m. Presumably, these per cent values are per cents by mass. The superconducting critical temperature was found to be 7.4 K for Tc + 22 % Sn, 7.1 K for Tc + 34 % Sn, and 6.4 K for Tc + 37 % Sn.

Both SnCl₂ and Sn(ClO₄)₂ reduce TcO₄⁻ to Tc(IV) species in acidic solutions (SM75, BB75, OM77, FM87). Reduction of TcO₄⁻ in aqueous HCl by SnCl₂ occurred initially to a Tc(V) species, and further reduction to Tc(IV) was much slower (SM75, BB75). This reduction to Tc(IV) can take several hours, especially if only a slight excess of SnCl₂ is used. These results give no evidence for technetium-tin complexes.

There is indirect evidence that Sn²⁺ or SnCl_x^{2-x} complexes form with technetium. For example, reduction of TcO₄⁻ in aqueous HCl containing potassium ferrocyanide gave a blue product when reduced with Bi(Hg) or Hg, but a yellowish-brown complex formed instead when SnCl₂ was used (A-KM62). The presence of SnCl₂ also affects biodistribution of some technetium radiopharmaceuticals (DF74). These facts suggest some kind of interaction between technetium and tin(II) may be occurring in some cases.

Evidence of a somewhat more direct nature exists for the presence of technetium complexes with SnCl_x^{2-x} . Steigman et al. (SM78) reduced technetium electrolytically to Tc(III) in a phosphate buffer. Addition of SnCl_2 caused no further reduction of technetium, but it did cause large changes in the absorption spectrum. They found similar evidence for association of SnCl_x^{2-x} with a mixed valence Tc(III,IV) phosphate complex. Kroesbergen et al. (KV86) studied $^{99\text{m}}\text{TcO}_4^-$ that was reduced by SnCl_2 in the presence of pyrophosphate ions. Absorption of these reduction products on solid $\text{Ca}_3(\text{PO}_4)_2$ at various pH values indicated that a negatively charged Tc-Sn-pyrophosphate complex was initially present. Either that complex or its dissociation products were absorbed on the $\text{Ca}_3(\text{PO}_4)_2$.

One solid complex of technetium with tin has been isolated and structurally characterized (DE76). It was prepared by addition of chlorostannic acid to a TcO_4^- solution in 95 % ethanol saturated with dimethylglyoxime. A brown product gradually formed. However, if water was added and the solution allowed to sit for several weeks, small amount of yellow crystals formed instead. A single crystal structural determination indicated that this complex was $[\text{Tc}(\text{dmg})_3(\text{SnCl}_3)(\text{OH})] \cdot 3\text{H}_2\text{O}$. It

crystallized in the triclinic space group P1 with $a = (11.471 \pm 0.001) \times 10^{-10}$, $b = (11.921 \pm 0.002) \times 10^{-10}$, $c = (10.811 \pm 0.002) \times 10^{-10}$ m, $\alpha = 65.13 \pm 0.02^\circ$, $\beta = 80.02 \pm 0.02^\circ$, $\gamma = 73.55 \pm 0.05^\circ$, and $Z = 2$. The tin atom effectively forms a three-pronged "cap" at one end of the Tc-dimethylglyoxime complex. Since the extent of protonation of the dmg in the complex is unknown, the charge on the Tc and Sn atoms is also unknown. From indirect evidence, they suggested this complex probably contained Tc(V) and Sn(IV) (DE76).

No thermodynamic data are available for these complexes of tin with technetium. However, they do not seem to be strong enough to survive under normal environmental conditions.

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Table 1. Crystal structural data for binuclear technetium chlorides.^a

Compound	Crystal Classification	Space Group	Z	10 ¹⁰ x a 10 ¹⁰ x b 10 ¹⁰ x c	Technetium Valence	Reference
$K_3[Tc_2Cl_8] \cdot 2H_2O^b$	trigonal	$P3_121$ (or $P3_221$)	3	12.80±0.05 12.80±0.05 8.30±0.04	2,3	KN72
$K_3[Tc_2Cl_8] \cdot nH_2O^b$	trigonal	$P3_121$ (or $P3_221$)	3	12.838±0.003 12.838±0.003 8.187±0.002	2,3	CS75
$K_8[Tc_2Cl_8]_3 \cdot (H_2O) \cdot 3H_2O^b$	trigonal	$P3_121$ (or $P3_221$)	1	12.80±0.05 12.80±0.05 8.30±0.04	2,3 (2 2/3 ave.)	KN75
$Cs_3[Tc_2Cl_8] \cdot 2H_2O^b$	trigonal	$P3_121$ (or $P3_221$)	3	12.90±0.05 12.90±0.05 8.70±0.04	2,3	KN72
$Cs_8[Tc_2Cl_8]_3 \cdot 2H_2O^b$	trigonal	$P3_121$ (or $P3_221$)	1	12.90±0.06 12.90±0.06 8.70±0.06	2,3 (2 2/3 ave.)	KN75
$(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$	trigonal	$P3_121$ (or $P3_221$)	3	13.03±0.02 13.03±0.02 8.40±0.01	2,3	CB65
$(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$	trigonal	$P3_121$ (or $P3_221$)	3	13.04±0.02 13.04±0.02 8.40±0.01	2,3	BC70

Table 1. continued

Compound	Crystal Classification	Space Group	Z	10^{10} x a 10^{10} x b 10^{10} x c	Technetium Valence	Reference
$Y[Tc_2Cl_8] \cdot 9H_2O$	tetrago- nal	$P4_212$ (or $P\bar{4}2_1m$)	4	11.712 ± 0.002 11.712 ± 0.002 7.661 ± 0.002	2,3	C082
$[(n-C_4H_9)_4N]_2[Tc_2Cl_8]$	Mono- clinic ^c	$P2_1/c$	(4)	10.922 15.384 16.439	3,3	SH77
$[(n-C_4H_9)_4N]_2[Tc_2Cl_8]$	Mono- clinic ^d	$P2_1/c$	4	10.915 ± 0.001 15.382 ± 0.003 16.409 ± 0.002	3,3	C081
$K_2[Tc_2Cl_6]$	Mono- clinic ^e	Cc	4	8.287 ± 0.002 13.956 ± 0.003 8.664 ± 0.002	2,2	KG86

^aUnits of a, b, and c are meters.

^bThese three potassium compounds are probably all $K_3[Tc_2Cl_8] \cdot nH_2O$ with $n \leq 2$; the cesium compounds are probably both $Cs_3[Tc_2Cl_8] \cdot nH_2O$ with $n \leq 2$.

^c $\beta = 122.37^\circ$

^d $\beta = 122.37 \pm 0.01^\circ$

^e $\beta = 93.99 \pm 0.05^\circ$

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