

Tetraphenylpyridinium pertechnetate: a promising salt for the immobilization of technetium

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Summary. In the context of the immobilization of technetium, as pertechnetate, from spent nuclear fuel from reprocessing activities, or potentially a scavenger for pertechnetate in repository conditions, the compound tetraphenylpyridinium pertechnetate (TPPy-TcO₄) has been synthesized, structurally characterized and its solubility investigated. The compound TPPy-TcO₄ has been prepared by metathesis from ammonium pertechnetate and 1,2,4,6-tetraphenylpyridinium tetrafluoroborate from a water/acetone media. Diffraction measurements show that the compound crystallizes in the orthorhombic space group (Pbca) with $a = 16.1242(10)$ Å, $b = 16.7923(10)$ Å, and $c = 17.6229(11)$ Å. The solubility of the salt has been investigated at room temperature in aqueous media at pH 2.22, 6.91, and 9.81 where solubility products were determined as 6.16×10^{-12} , 4.13×10^{-12} , and 1.16×10^{-11} , respectively. The compound TPPy-TcO₄ is not the most insoluble pertechnetate salt reported so far, but comparatively has a lower solubility than that of most other pertechnetate salts.

1. Introduction

Pertechnetate complexes are mainly encountered in the medical and nuclear industry. Typically ^{99m}TcO₄⁻ is used as precursor for the synthesis of radio-imaging agents while ⁹⁹Tc is a major fission product of the nuclear industry where TcO₄⁻ is formed during the reprocessing of spent nuclear fuel. Advanced recycling processes have been under consideration to separate transuranic elements from spent nuclear fuel. The first step of these processes is the dissolution of spent fuel in nitric acid which produces the pertechnetate anion. Following, TcO₄⁻ can be extracted with uranium, as uranyl, into an organic phase consisting of 30% TBP diluted in dodecane [1–8]. Treatment of the resulting stream requires the separation of Tc from U. Once separation is achieved, technetium has been envisioned to be converted to the metal and incorporated into a metallic alloys [9] for future waste management [10]. Other types of waste forms have also been proposed [11] which can require thermal treatment of the pertechnetate anion, whereas ultimately Tc exposed to the environment of a hypothetical repository will

ultimately be dominated by the solubility of TcO₄⁻ [12]. Large cations of pertechnetate salts have very low solubilities; these could be used as an alternative matrix for Tc immobilization. Furthermore, their synthesis does not require thermal treatment or significant handling in regards to the formation of the precipitate.

Previously, work has shown that trialkylammonium cations interact with pertechnetate and can be used for Tc separation in the reprocessing of spent fuel [13]. Further studies have shown that the solubility of TcO₄⁻ salts is related to the cations size: larger cation are shown to lower the solubility of these compounds [14]. The large tetraphenylpyridinium cation (TPPy) has already been used in the preparation of the insoluble ($K_{sp} = 1.35 \times 10^{-10}$ at pH = 11.6, 1.0 M NH₃, 0 M NaCl 20 °C) TPPy-perrhenate salt [15] while the technetium homologue had not been reported. Here, we report on the synthesis and characterization while investigating the solubility properties of the TPPy-pertechnetate salt.

2. Experimental

Technetium-99 is a weak β emitter ($E_{max} = 292$ keV). All manipulations were performed in a laboratory designed for radioactivity using efficient HEPA-filtered fume hoods, Schlenk and glovebox techniques while following locally approved radiochemistry handling and monitoring procedures. Laboratory coats, disposable gloves, and protective eyewear were worn at all times.

2.1 Reagents

Ammonium pertechnetate was purchased from Oak Ridge National Laboratory and purified according to the method reported in the literature [16]. Tetraphenylpyridinium tetrafluoroborate (TPPy-BF₄) was purchased from sigma-aldrich and used as received.

2.2 Synthesis

The compound TPPy-TcO₄ was precipitated from a solution of NH₄TcO₄ using TPPy-BF₄ in a 1.02 : 1.00 mol ratio (TcO₄⁻ : TPPy). The compound TPPy-BF₄ (100.3 mg, 0.251 mmol) was dissolved in 1 ml acetone and placed in a 15 ml centrifuge tube. A solution of ammonium pertechnete-

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tate (44.5 mg, 0.246 mmol) in water was added to the TPPy-BF₄ whereupon a white solid immediately precipitated. The precipitate was centrifuged for 5 min and the supernatant removed. The precipitate was washed 3 × with 5 ml of water followed by 3 × with 5 ml of diethyl ether and allowed to dry for 24 h under air. The resulting TPPy-TcO₄ solid (93.9 mg, yield = 80.6%) was characterized by diffraction techniques and used for solubility experiments.

2.3 Single crystal XRD (SCXRD) and powder XRD measurements

Single crystals suitable for SCXRD were grown in methanol for 3 days at −25 °C. Data was collected on a Bruker Apex II system equipped with an Oxford nitrogen cryostream operating at 150 K. Crystals were mounted under paratone on a glass fiber. Data processing was performed using the Apex II suite, and an absorption correction performed with SADABS. Structure solution (Direct Methods) and refinement were carried out using SHELX97. The structure was solved with SIR2004 [17] within the WINGX program suite [18]. Following structure solution, the model was refined against F² using SHELXTL [19]. Hydrogen atoms were inserted using the riding model, and the refinement proceeded smoothly, yielding a structure model with a 2.77% R₁ value¹. The XRD patterns were obtained using a Philips Panalytical X'Pert Pro, Cu K_α target with Ni filter and an X'elerator multiple Si-strip solid-state detector. The XRD patterns were quantified by Rietveld analysis using the Topas 3.0 software [20].

2.4 Solubility measurements

The Solubility of TPPy-TcO₄ was evaluated by massing 5 mg of TPPy-TcO₄ into a 20 mL glass scintillation vial and filled with 15 ml of solution adjusted to pH = 2.22 (HNO₃), pH = 6.91 (Boiled and de-aerated 18 MΩ cm DI H₂O) and pH = 9.81 (NaOH) held at 17 °C. The solution pH was determined using a Thermo, Orion 3 STAR benchtop pH meter. The vials were closed and left undisturbed for 60 d with intermediate aliquots removed. To determine the quantity of soluble Tc(VII) in solution, 100 μl aliquots were removed from the vials using a calibrated pipette, diluted to 1 ml in DI H₂O and passed through a 0.45 μm filter to remove particulates potentially suspended in solution. Following, 100 μl of the resulting solutions were added to 10 mL of scintillation cocktail and concentrations determined by liquid scintillation (LS) counting. ⁹⁹Tc concentrations evaluated by LS counting used a Packard 2500 scintillation analyzer. The scintillation cocktail used was ULTIMA GOLD AB™ (Packard). The concentrations of solutions were determined using calibration curves performed in solution with a composition similar to the experimental parameters.

3. Results and discussion

3.1 Synthesis

There are approximately fifty pertechnetate salts known to date with formula A·[TcO₄]_n (A = alkaline metal, transition

metal, rare earth, trialkylammonium, *n* = 1 to 3) [21, 22]. TPPy-TcO₄ is the first pertechnetate salt with a pyridinium cation to be structurally characterized. The compound was synthesized at an 81% yield from pertechnetate by precipitation with TPPy-BF₄ from the water-acetone solution. After the initial precipitation, further compound can be recovered from the remaining acetone-water solution by evaporation and yields are nearly quantitative. This method differs from the one reported for rhenium which used precipitation by TPPy-acetate [15] and was developed due to the availability and insolubility of the TPPy-BF₄ salt in water. Analysis of the precipitate by powder XRD shows the sample to contain only the TPPy-TcO₄ phase. The compound is air stable and can be kept for months without apparent degradation. Like other pertechnetate salts, the stability of the compound is determined by the stability of the cation. Under inert atmosphere, TPP-TcO₄ is stable to approximately 300 °C until it decomposes forming a non-radioactive volatile yellow oil and a black, non-diffracting XRD amorphous, compound. Preliminary studies indicate that TPPy-TcO₄ is soluble in acetone, slightly soluble in methanol and is insoluble in diethyl ether and water.

3.2 Structure

The compound TPPy-TcO₄ (Fig. 1) crystallizes in the orthorhombic space group (Pbca). The cell parameter (*a* = 16.1242(10) Å, *b* = 16.7923(10) Å, *c* = 17.6229(11) Å) is larger than in any other pertechnetate salts [23].²

Analysis of structural parameters in the pertechnetate anion shows a small disparity of the Tc=O bond distances (from 1.709(1) Å to 1.724(1) Å) in comparison to the one observed in the trialkylammonium salts (*i.e.*, [Bu₄N]TcO₄ [21] Tc=O varying from 1.58 Å and 1.706 Å). Disparity of Tc=O distance in pertechnetate salts has been discussed and is due to various effect such as: size of unit cell or polarizability of the cation. In our case, a large unit

² These values are in agreement with the one found by powder XRD (*a* = 16.3500(21) Å, *b* = 16.9278(24) Å, *c* = 17.72790(70) Å).

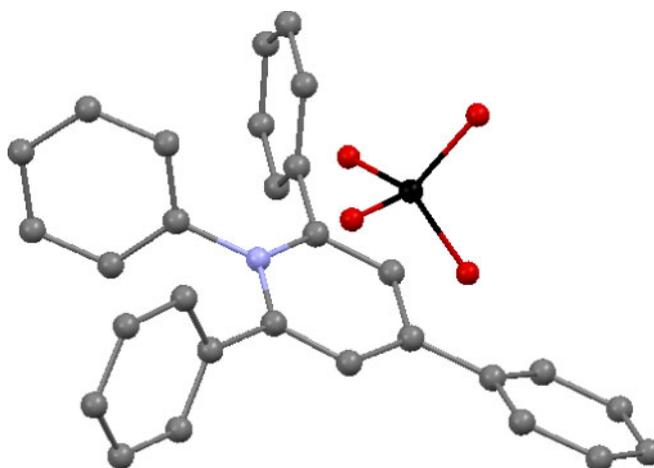


Fig. 1. Ball and stick representation of TPPy-TcO₄ showing the pertechnetate anion and the larger TPPy cation. Distances are in Å. Hydrogen atoms are omitted for clarity.

¹ Additional structural parameter and cif file are provided in supporting information.

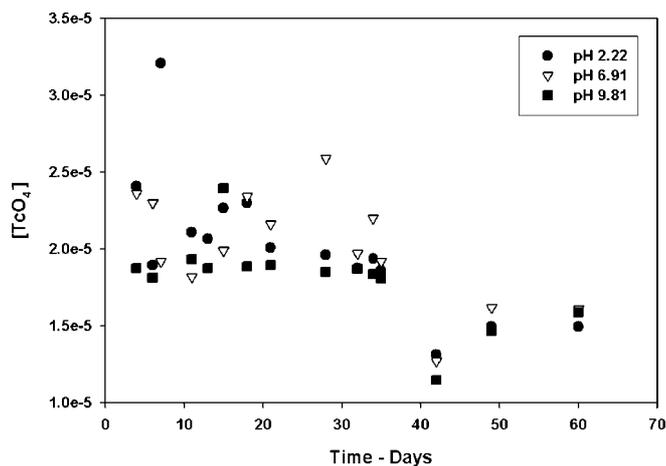


Fig. 2. Molar concentration of TcO_4^- , as a function of time in solution at pH 2.22, 6.91 and 9.81.

cell (4771.62 \AA^3) combined with a low polarizability³ of the TPPy cation is likely to be the origin of the small disparity of the $\text{Tc}=\text{O}$ distance in TPPy- TcO_4 .

In the solid, the pertechnetate anion is surrounded by three cations, the shorter $\text{Tc}=\text{O}\cdots\text{H}$ distances (*i.e.*; 2.47, 2.50, 2.56 and 2.59 \AA) are less than the sum of the Van der Waals radius (2.60 \AA) and thus indicates that TcO_4^- is involved in hydrogen bonding with the cation [23]. Also, the shortest distance between the cations ($\text{C}\cdots\text{H} = 2.84 \text{ \AA}$) is slightly less than the Van der Waals radius (2.9 \AA) and indicates that TPPy is involved in hydrogen bonding, forming a network in the crystal. Extensive hydrogen bonding coupled to a low polarizability of the TPPy cation is likely to be responsible for the low solubility of the TPPy- TcO_4 salt.

3.3 Solubility

The solubility of TPP- TcO_4 was measured at room temperature in aqueous media at pH 2.22, 6.91 and 9.81 over a period of 60 days. Significant scatter is due to large changes in the temperature of the static bath TPPy- TcO_4 was exposed to during periodic air conditioning outages prior to reporting K_{sp} . The technetium concentrations (Fig. 2) reached a plateau after several days which indicates that the system reached its equilibrium solubility from which the estimated K_{sp} values were determined. The solubility values (Table 1) indicate TPPy- TcO_4 to be one of the most insoluble pertechnetate salts reported and in comparison and is lower than that reported for TPPy- ReO_4 [15].

Previous works have correlated the solubility of a TcO_4^- salt as a function of the polarizability of the cation. The representation of the solubility of pertechnetate salts as function of polarizability of the tetramethyl ammonium (TMA), tetraethyl ammonium (TEA), tetrabutyl ammonium (TBA) and TPPy cations (Fig. 3) shows a linear correlation. This indicates that physico-chemical behavior of TPPy- TcO_4 can be correlated to the one of the trialkylammonium salts and that polarization could be used as a parameter to predict solubility of other pyridinium pertechnetate salts.

³ Polarizability is defined as Z/R with Z charge and R radius of the cation; radius of TPPy 6.5 \AA was determined crystallographically.

Table 1. Estimated K_{sp} values of TPPy- TcO_4 .

pH	Conc [TcO_4^-]	Est. K_{sp}	Count error	Temp. °C
2.22	1.50×10^{-5}	2.24×10^{-10}	$\pm 2.0\%$	17
6.91	1.61×10^{-5}	2.59×10^{-10}	$\pm 1.8\%$	17
9.80	1.59×10^{-5}	2.51×10^{-10}	$\pm 1.8\%$	17

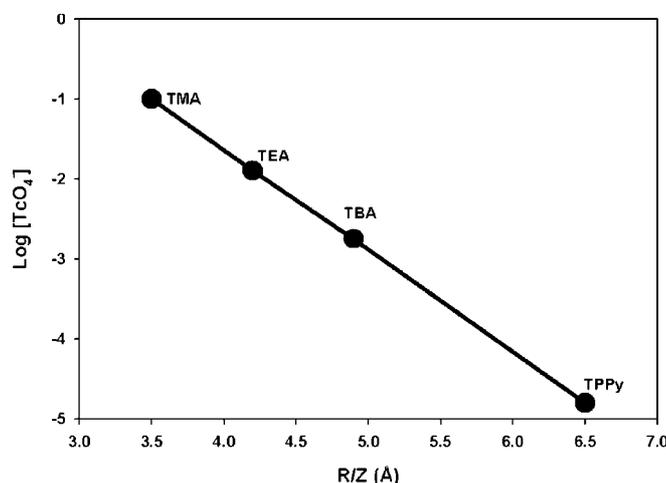


Fig. 3. Variation of $\log[\text{TcO}_4^-]$ as a function of the R/Z for the pertechnetate salts with the TMA, TEA, TBA and TPPy salts. Value for TMA, TBA and TEA are taken from literature [22].

Concerning the immobilization of technetium, we note that solubility of TPPy- TcO_4 is higher than the dioxide; solubility of TcO_2 over a pH range of 6 to 13 was estimated as 1×10^{-7} to as low as $3.2 \times 10^{-9} \text{ mol dm}^{-3}$ [12]. This indicates that the TPPy-cation could not be envisaged as a useful long-term waste form but would be better used as a pertechnetate scavenger in the near field of waste forms directly containing pertechnetate or one which would release pertechnetate as a corrosion or degradation product. Despite the form used in this study requiring the use of a water/acetone solution to precipitate and form the TPPy- TcO_4 compound, this cannot be used in environmental conditions as a starting form to scavenge Tc. We therefore would suggest the use of the TPPy-Acetate which would be a much more suitable form because it is fully soluble in water.

4. Conclusion

The new tetraphenylpyridinium (TPPy) pertechnetate salt has been synthesized by metathesis from NH_4TcO_4 and TPPy- BF_4 . Analysis of the TPPy- TcO_4 structure indicates that the pertechnetate anion is not distorted as is observed in the trialkylammonium salts, and shows the presence of extensive hydrogen bonding in the solid. The polarizability of the TPPy cation is responsible for the low solubility of this salt, which could find applications for Tc regarding management of spent fuel. Though the use of TPPy- TcO_4 may not have noteworthy uses as a waste form that will contain Tc for extended periods of time, its use as an intermediate for scavenging or precipitating Tc selectively may find notoriety in environmental recovery of Tc.

Its use may also extend to separations requiring isolation of Tc from other anions in solution not precipitated by TPPy. Current efforts are focused on the synthesis of other insoluble pertechnetate salts, in this context, we note that bis(triphenylphosphin)iminium pertechnetate salt has yet to be reported. In the future we propose to study the TPPy-TcO₄, and other Tc(VII) salts under gamma irradiation to further understand how this type of induced degradation may affect the overall stability and solubility of this and other compounds.

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