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Identification of the Non-pertechnetate Species in Hanford Waste Tanks, Tc(I) Carbonyl Complexes

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ABSTRACT Immobilization of the high-level nuclear waste stored at the Hanford Reservation has been complicated by the presence of soluble, lower-valent technetium species. Previous work by Schroeder and Blanchard has shown that these species cannot be removed by ion-exchange and are difficult to oxidize. The Tc-K edge XANES spectra of the species in Tanks SY-101 and SY-103 were reported by Blanchard, but they could not be assigned to any known technetium complex. We report that the XANES spectra are most likely those of Tc(I) carbonyl species, especially *fac*-Tc(CO)₃(gluconate)²⁻. This is further supported by EXAFS and ⁹⁹Tc-NMR studies in nonradioactive simulants of these tank wastes.

KEYWORDS Technetium, Hanford, high level waste, nuclear waste

BRIEFS The soluble technetium species that have caused problems for the remediation of high level nuclear waste at Hanford are most likely Tc(I) carbonyl complexes.

MANUSCRIPT TEXT:

Introduction. The Hanford Reservation in eastern Washington State is the site of one of the largest and most costly remediation efforts in the U.S. Years of plutonium production have generated 53 million gallons of nuclear waste, which is now located in 177 underground tanks.¹ The current plan for immobilizing this waste involves separating it into high and low activity streams, which will be vitrified separately to form high and low activity waste glasses.¹ The low activity waste stream mainly consists of the water-soluble fraction of the waste, which includes high concentrations of sodium hydroxide, nitrate and nitrite and the radionuclides ¹³⁷Cs, ⁹⁹Tc, and ⁹⁰Sr. The high activity waste stream chiefly contains insoluble iron oxides, aluminosilicates, and oxides of the actinides and fission products. Due to the performance requirements for the low activity waste glass, almost all of the ¹³⁷Cs and ⁹⁰Sr and approximately 80% of the technetium (⁹⁹Tc) must be removed from the low activity waste stream and sent to the high activity waste stream.^{2,3} The procedure for removing technetium was ion exchange of pertechnetate, TcO₄⁻, the most thermodynamically stable form of technetium at high pH. While ion exchange is effective for many tanks, it fails for Complexant Concentrate (CC) waste tanks, including tanks SY-101 and SY-103, which contain the organic complexants nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), citrate, and gluconate.^{4,5} In these tanks, the majority of technetium is present as a soluble, lower-valent, non-pertechnetate species that is not removed during pertechnetate ion exchange.⁴

The identity of this species is unknown, but its behavior is intriguing and has hampered efforts to remove it. It is not readily removed by ion exchange, and although the non-pertechnetate species is air-sensitive (it slowly decomposes to pertechnetate), it is difficult to oxidize in practice.^{4,6} The only spectroscopic characterization of the non-pertechnetate species is a series of Tc K-edge X-ray absorption near edge structure (XANES) spectra of CC samples reported by Blanchard, et al. (Fig. 1).⁶ Although its identity could not be determined from these spectra, the non-pertechnetate species was believed to be Tc(IV) based

upon the energy of its absorption edge, which occurs at 7 eV lower than that of TcO_4^- . This energy is similar to that of TcO_2 , which is 7 eV lower than that of TcO_4^- .⁷

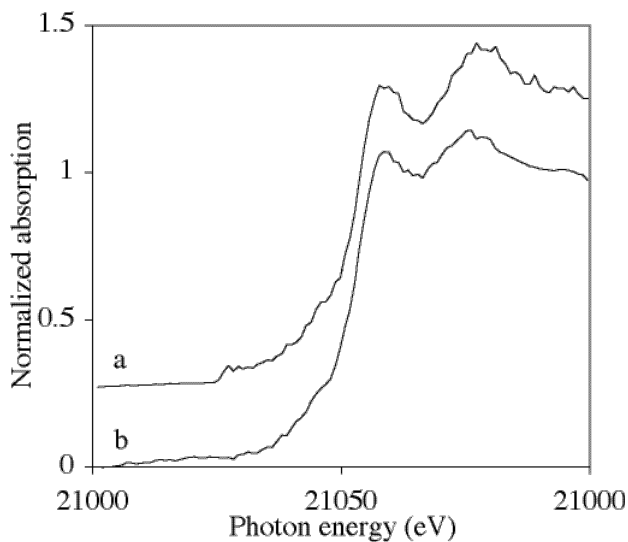


Figure 1. Tc K-edge XANES spectra of the non-pertechnetate species in tanks a) SY-103, b) SY-101 reported by Blanchard and coworkers in Ref. ⁶.

Identification of the non-pertechnetate species has been complicated by the fact that the ligands present in CC waste form few lower valent technetium complexes that are hydrolytically stable in strongly alkaline solution. While Tc(IV) aminopolycarboxylate complexes are well-known and stable towards oxidation,^{8,9} they decompose to form $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ in alkaline solution.¹⁰ However, a number of Tc(IV) alkoxide complexes are stable in alkaline solution,^{11,12} and previous studies have shown that stable Tc(IV) alkoxide complexes can be formed by radiolysis in alkaline solution.¹⁰ However, the alkoxides examined in previous studies are not present in sufficient quantities in CC waste to account for the amount of non-pertechnetate species found in tanks SY-101 and SY-103. We report the results of XANES, extended X-ray absorption fine structure (EXAFS), and ⁹⁹Tc-NMR studies on lower valent technetium complexes that are potentially present in CC waste.

Experimental procedures. *Caution:* ⁹⁹Tc is a β^- -emitter ($E_{max} = 294 \text{ keV}$, $T_{1/2} = 2 \times 10^5 \text{ years}$). All operations were carried out in a radiochemical laboratory equipped for handling this isotope. Technetium, as $\text{NH}_4^{99}\text{TcO}_4$, was obtained from Oak Ridge National Laboratory. The solid $\text{NH}_4^{99}\text{TcO}_4$ was

contaminated with a large amount of dark, insoluble material. Prolonged treatment of this sample with H_2O_2 and NH_4OH did not appreciably reduce the amount of dark material. Ammonium pertechnetate was separated by carefully decanting the colorless solution from the dark solid. A small amount of NaOH was added to the colorless solution, and the volatile components were removed under vacuum. The remaining solid was dissolved in water, and the colorless solution was removed from the remaining precipitate with a cannula. The concentration of sodium pertechnetate was determined spectrophotometrically at 289 nm ($\epsilon = 3800 \text{ mol}^{-1} \text{ cm}^{-1}$). UV-visible spectra were obtained using an Ocean-Optics ST2000 spectrometer. NMR spectra were recorded using a JEOL FX-90Q FT NMR spectrometer equipped with a Tecmag Libra data acquisition system. X-ray absorption fine structure (XAFS) spectra were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) at Beamline 4-1 or 11-2 using a Si(220) double crystal monochromator detuned 50% to reduce the higher order harmonic content of the beam. XAFS spectra were obtained in fluorescence yield mode using a multi-pixel Ge-detector system.¹³ The spectra were energy calibrated using the first inflection point of the pre-edge peak from the Tc K edge spectrum of an aqueous solution of NH_4TcO_4 defined as 21044 eV. To determine the Tc K edge charge state shifts, the energies of the Tc K edges at half height were used. The EXAFS analysis was performed as previously described.¹⁰

All operations were carried out in air except as noted. Water was purified by a MilliQ system. All other chemicals were used as received. $\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3^+$ stock solution was prepared from $\text{TcOCl}_4(\text{n-Bu}_4\text{N})$ ¹⁴ by the procedure developed by Alberto¹⁵ and then dissolving the reaction product in 0.01M triflic acid. The ⁹⁹Tc concentration was determined by liquid scintillation.

Solutions for NMR experiments were prepared by addition of 0.10 mL aliquots of the $\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3^+$ stock solution to 0.90 mL of 1.1M NaOH in D_2O with and without 0.11M organic complexant. NMR samples were contained inside Teflon tubes inside 10 mm screw cap NMR tubes. The SY-101 simulant is the following: 3.78M NaOH , 1.09M NaNO_2 , 0.42M $\text{Al}(\text{NO}_3)_2$, 0.058M NaF , 0.037M Na_2CO_3 , 0.034M KF , 0.031M Iminodiacetic Acid, 0.02M Na_2HPO_4 , 0.013M Na_2EDTA , 0.012M Potassium Gluconate, 0.005M Sodium Citrate, 0.005M Na_2SO_4 , 0.004M $\text{Ca}(\text{NO}_3)_2$, 0.0005M $\text{Zn}(\text{NO}_3)_3$, 0.0002M Na_3NTA , 0.0002M $\text{Ni}(\text{NO}_3)_2$, and 0.0002M $\text{Fe}(\text{NO}_3)_3$. Solutions for XAFS spectroscopy were prepared by addition of 0.20 mL aliquots of the $\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3^+$ stock solution to 0.80 mL of 1.1M NaOH in D_2O

with and without 0.11M organic complexant. The Tc(IV) gluconate complex was prepared by reducing a solution of TcO_4^- (2mM, 1 mL, 2 μmol) in 0.1M potassium gluconate and 1M NaOH with sodium dithionite (2M, 10 μL , 20 μmol). Solutions were sealed under Ar inside 2 mL screw-cap centrifuge tubes inside two consecutive heat sealed, heavy walled polyethylene pouches. Samples were stored under Ar in glass jars sealed with PTFE tape and were removed at the beamline just prior to initiation of experiments.

Results and discussion. Previous work aimed at understanding the formation of the soluble non-pertechnetate species in Hanford high level nuclear waste showed that Tc(IV) alkoxide complexes can be formed under the conditions present in CC waste. Since one component of CC waste, gluconate, is a polyol, Tc(IV) gluconate is a likely candidate for the soluble, non-pertechnetate species. However, as shown in Fig. 2, the XANES spectrum of Tc(IV) gluconate is different from that of the non-pertechnetate species, and the spectrum of the non-pertechnetate species cannot be fit using the spectra of Tc(IV) gluconate, Tc(V) gluconate, and pertechnetate. Furthermore, the energy of the X-ray absorption edge of Tc(IV) gluconate, 5.5 eV lower than that of TcO_4^- , does not agree with that of the non-pertechnetate species. Based upon this large difference in absorption edge shift, the non-pertechnetate species in CC waste is not a simple Tc(IV) alkoxide complex.

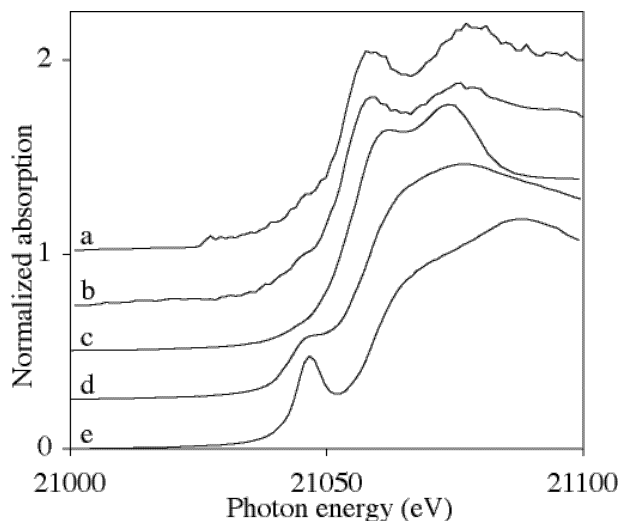


Figure 2. Tc K-edge XANES spectra of a) non-pertechnetate species in tank SY-103, b) non-pertechnetate species in tank SY-101, c) Tc(IV) gluconate, d) Tc(V) gluconate, e) TcO_4^- . The spectra of the non-pertechnetate species in tanks SY-101 and SY-103 are from Ref. ⁶.

To identify potential candidates for the non-pertechnetate species, the XANES spectra of the non-pertechnetate species were compared to theoretical XANES spectra calculated¹⁶ for several lower-valent technetium species that could be stable in alkaline solution, regardless of whether the ligands are present in CC waste. Surprisingly, the best candidate was the Tc(I) carbonyl complex, *fac*-Tc(CO)₃(H₂O)₃⁺, shown in Fig. 3. This complex, and derivatives in which the coordinated water molecules are replaced by other ligands, have received considerable attention since they show great promise as ^{99m}Tc radiopharmaceuticals; consequently, their synthesis and solution behavior have studied in detail.^{15,17-19} Of particular interest is the fact that *fac*-Tc(CO)₃(H₂O)₃⁺ can be prepared at tracer concentrations in alkaline aqueous solution under conditions that are very similar to CC waste including low CO concentration.^{18,19} Furthermore, *fac*-Tc(CO)₃⁺ forms hydrolytically stable complexes in alkaline solution, including the simple hydroxide complexes *fac*-Tc(CO)₃(HO)(H₂O)₂ and *fac*-Tc(CO)₃(HO)₂(H₂O)⁻²⁰. The similar Tc(I) dicarbonyl nitrosyl complex Tc(CO)₂(NO)(H₂O)₃²⁺ in which one CO ligand has been replaced by the isoelectronic NO⁺ ligand has also been reported.²¹ To determine the behavior of *fac*-Tc(CO)₃⁺ complexes in the presence of components of CC waste, *fac*-Tc(CO)₃(H₂O)₃⁺¹⁵ was added to solutions of 1M NaOH or 0.1M EDTA, citrate, or gluconate in 1M NaOH and their Tc K-edge XANES and EXAFS and ⁹⁹Tc NMR spectra were examined.

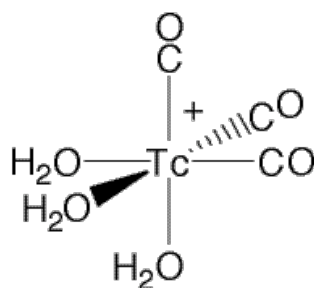


Figure 3. Structure of *fac*-Tc(CO)₃(H₂O)₃⁺.

The XANES spectra of *fac*-Tc(CO)₃ complexes are shown in Fig. 4 along with the spectra of the non-pertechnetate species in tanks SY-101 and SY-103. Neither citrate nor EDTA forms a complex *fac*-Tc(CO)₃ with in 1M NaOH since the spectrum of *fac*-Tc(CO)₃ in 0.1M citrate or EDTA and 1M NaOH was identical to that in 1M NaOH alone, which results from *fac*-Tc(CO)₃(HO)(H₂O)₂.²⁰ The Tc K absorption edges of *fac*-Tc(CO)₃(HO)(H₂O)₂ and *fac*-Tc(CO)₃(gluconate)²⁻ occur at 7.5 eV and 7.3 eV below that of TcO₄⁻, respectively, similar to that of the non-pertechnetate species. More importantly,

the XANES spectra of the non-pertechnetate species can be fit using the XANES spectrum of $\text{Tc}(\text{CO})_3(\text{gluconate})^{2-}$ (along with 7% TcO_4^- for tank SY-101 to account for sample decomposition). The XANES spectra can also be fit using *fac*- $\text{Tc}(\text{CO})_3(\text{HO})(\text{H}_2\text{O})_2$, but the fit quality is slightly poorer.

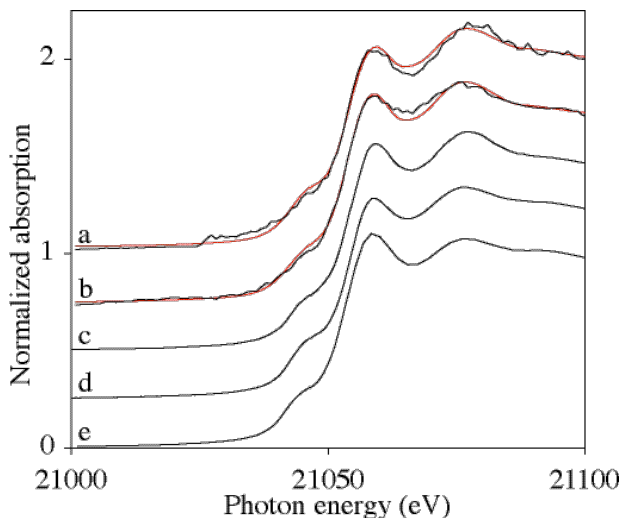


Figure 4. Tc K-edge XANES spectra of a) non-pertechnetate species in tank SY-103 (black) and $\text{Tc}(\text{CO})_3(\text{gluconate})^{2-}$ (red), b) non-pertechnetate species in tank SY-101 (black) and 93% $\text{Tc}(\text{CO})_3(\text{gluconate})^{2-}$ with 7% TcO_4^- (red), c) $\text{Tc}(\text{CO})_3(\text{gluconate})^{2-}$, d) $\text{Tc}(\text{CO})_3(\text{HO})(\text{H}_2\text{O})_2$, e) $\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3^+$. The spectra of the non-pertechnetate species in tanks SY-101 and SY-103 are from Ref. 14

As noted above, analogous Tc(I) dicarbonyl nitrosyl complexes, including $\text{Tc}(\text{CO})_2(\text{NO})(\text{H}_2\text{O})_3^{2+}$, are known.²¹ The $\text{Tc}(\text{CO})_2(\text{NO})$ complexes are somewhat more stable than *fac*- $\text{Tc}(\text{CO})_3$ complexes and could be generated in high level waste as a result of the radiolytic decomposition of nitrate and nitrite.^{22,23} The XANES spectra of $\text{Tc}(\text{CO})_2(\text{NO})$ and *fac*- $\text{Tc}(\text{CO})_3$ would be similar. Given the similarity of the XANES spectra of the Tc(I) carbonyl complexes, assignment of the non-pertechnetate species to a particular species is not conclusive although $\text{Tc}(\text{CO})_3(\text{gluconate})^{2-}$ provides an excellent fit to the observed XANES spectrum of the non-pertechnetate species.

The structures of Tc(IV) gluconate and selected *fac*- $\text{Tc}(\text{CO})_3$ complexes were characterized by EXAFS. Fig. 5 shows the EXAFS spectra of Tc(IV) gluconate. The structural parameters obtained by fitting the spectra are given in Table 1. The EXAFS spectrum and coordination environment of the Tc(IV) gluconate

complex are simple; the Tc center has six oxygen ligands at 2.01 Å, typical of a Tc(IV) alkoxide.¹² The carbon atoms to which the coordinated oxygen ligands are bound are 2.37 Å from the Tc center with a fairly large Debye-Waller factor of 0.015 Å². Although the geometry of the coordinated gluconate cannot be determined with certainty from these results, the large Debye-Waller factor for the carbon atoms is consistent with coordination by the carboxylate and two hydroxyl groups of the gluconate ligand (rather than three hydroxyl groups), which gives the Tc(IV) gluconate complex the formula Tc(gluconate)₂²⁻. This coordination geometry of gluconate is illustrated in Fig. 5 and is similar to that of calcium lactobionate except that that the hydroxyl groups are deprotonated in Tc(gluconate)₂²⁻. The most similar technetium complex is the tris(hydroxymethyl)(trimethylammino)methane complex of Tc(IV), which consists of a Tc(IV) center coordinated by two tridentate alkoxide ligands with an average Tc-O bond length of 2.00(1) Å.¹²

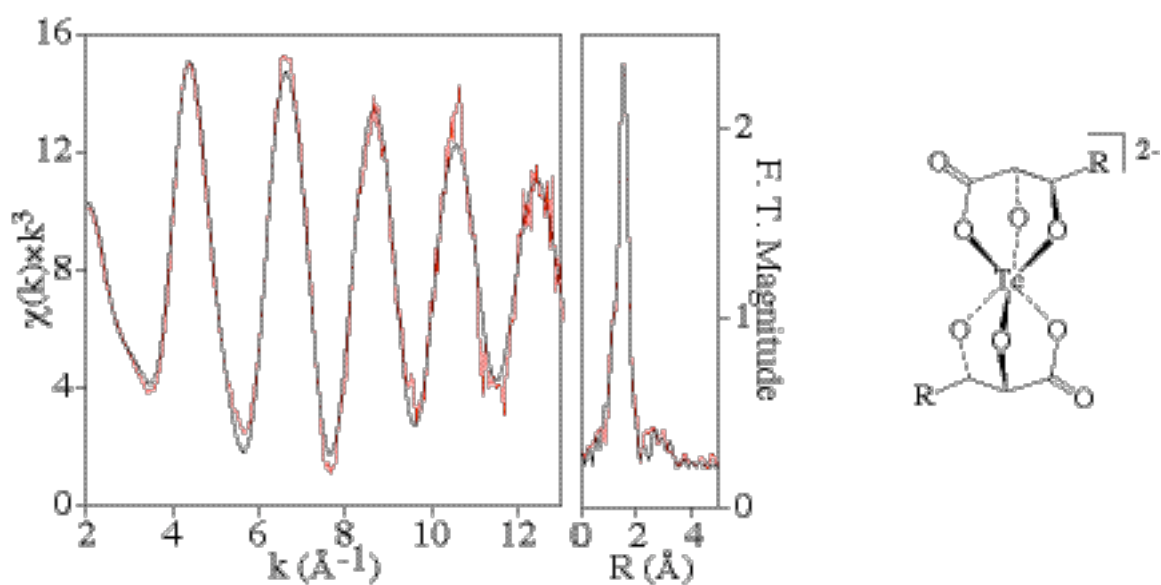


Figure 5. EXAFS spectrum and Fourier transform (left panels) of Tc(gluconate)₂²⁻; data are illustrated in red, least squares fits are black. Proposed structure consistent with the EXAFS data is illustrated to the right where R=C₃H₄(OH)₃.

Table 1. EXAFS fitting results for Tc complexes

Scattering Path		Complex			
		Tc(gluconate) ₂ ²⁻	Tc(CO) ₃ (H ₂ O) ₃ ⁺	Tc(CO) ₃ (H ₂ O) ₂ (OH)	Tc(CO) ₃ (gluconate) ₂ ²⁻
Tc-CO	N		3	3	3
	R(Å)		1.904(2)	1.886(3)	1.911(2)
	σ ² (Å ²)		0.0041(2)	0.0058(3)	0.0062(2)
Tc-O	N	6	3	3	3
	R(Å)	2.010(1)	2.163(2)	2.155(3)	2.137(2)
	σ ² (Å ²)	0.0045(1)	0.0052(2)	0.0047(5)	0.0068(3)
Tc-CO ^a	N		3	3	3
	R(Å)		3.045(9)	3.083(8)	3.09(3)
	σ ² (Å ²)		0.0050(2)	0.0046(2)	0.0015(2)
Tc-OC	N	6			3
	R(Å)	3.37(2)			3.44(2)
	σ ² (Å ²)	0.015(3)			0.011(2)
4 leg MS path due to <i>trans</i> ligands coordinated to Tc	N	6	6	6	6
	R(Å)	4.03(2)	3.96(2)	4.01(2)	3.96(1)
	σ ² (Å ²)	0.008(3)	0.017(4)	0.010(3)	0.019(3)
□E ₀		-5.2(3)	-14.8(4)	-11.6(6)	-11.1(3)
Scale Factor		1.38(3)	1.39(4)	1.19(6)	1.68(7)

a) This scattering path includes two additional multiple scattering paths that were constrained to have the same parameters as those given in the table.

The EXAFS spectra (Fig. 6) and structural parameters (Table 1) of the *fac*-Tc(CO)₃ complexes are all similar since the main differences among these complexes are the bond distances. The complex with the weakest σ and π-donor ligands is *fac*-Tc(CO)₃(H₂O)₃⁺; consequently, it has the longest Tc-O distance and the shortest CO distance, 1.14(1) Å. When a single water ligand is replaced by a hydroxide ligand in *fac*-Tc(CO)₃(HO)(H₂O)₂, the average Tc-O distance is reduced and the CO distance is increased to 1.20(1) Å as hydroxide is a stronger σ and π-donor ligand than water. In *fac*-Tc(CO)₃(gluconate)₂²⁻, the average Tc-O distance is still shorter, and the CO distance in *fac*-Tc(CO)₃(gluconate)₂²⁻ is 1.18(1) Å, which is comparable to that in *fac*-Tc(CO)₃(HO)(H₂O)₂. The Tc-OC and Tc-O distances are slightly longer than those of Tc(gluconate)₂²⁻ as expected for the larger Tc(I) ion, and the gluconate is assumed to be bound to the Tc center by the carboxylate and two hydroxyl groups as in Tc(gluconate)₂²⁻. A variety of *fac*-Tc(CO)₃ complexes have been examined previously by EXAFS, and the Tc-CO parameters are similar to those reported here.^{24,25} A similar complex that has been crystallographically characterized is the complex of *fac*-Tc(CO)₃ with the tripodal Kläui ligand cyclopentadienyltris(diethylphosphito)cobaltate, which has an average Tc-CO distance of 1.86(2) Å and a Tc-O distance of 2.17(1) Å.²⁶

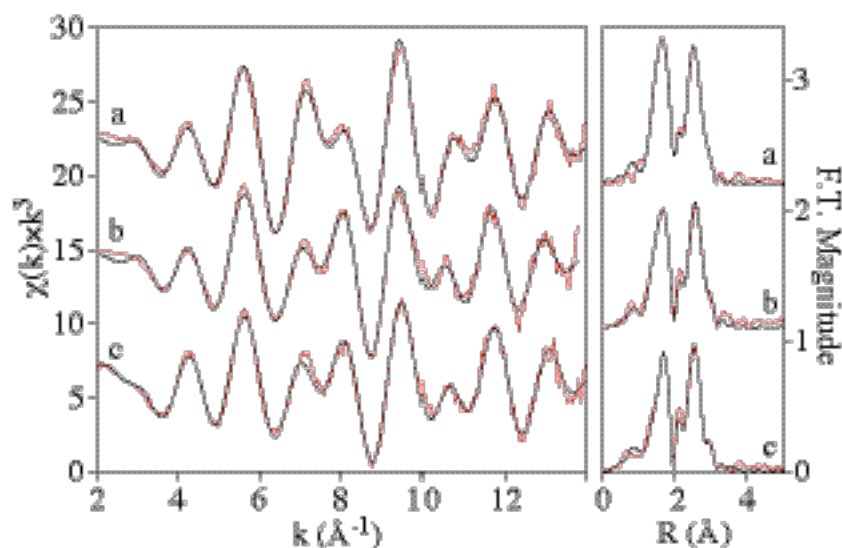


Figure 6. EXAFS spectra (left) and Fourier transforms (right) of a) *fac*-Tc(CO)₃(H₂O)₃⁺, b) *fac*-Tc(CO)₃(HO)(H₂O)₂, and c) *fac*-Tc(CO)₃(gluconate)²⁻. Data are illustrated in red, and least squares fits are black.

The ⁹⁹Tc NMR spectra of the *fac*-Tc(CO)₃ complexes are in good agreement with the XAFS data and allow the unambiguous assignment of the XANES and EXAFS spectra of the model complexes. Solutions of 5mM *fac*-Tc(CO)₃ in 1M NaOH with or without 0.1M EDTA or citrate showed a single resonance at -1060 ppm, which has previously been assigned to *fac*-Tc(CO)₃(HO)(H₂O)₂.²⁰ However, solutions of 5mM *fac*-Tc(CO)₃ in 1M NaOH with 0.1M gluconate had a single, broad ⁹⁹Tc resonance at -1239 ppm (Δ_{1/2} = 150Hz), which can be assigned to Tc(CO)₃(gluconate)²⁻. Solutions of 5mM *fac*-Tc(CO)₃ in an SY-101 simulant initially contained both *fac*-Tc(CO)₃(HO)(H₂O)₂ and *fac*-Tc(CO)₃(gluconate)²⁻, but after one week, only pertechnetate and *fac*-Tc(CO)₃(gluconate)²⁻ were present.⁵ In all of the NMR experiments, the *fac*-Tc(CO)₃ complexes showed slight decomposition to TcO₄⁻ after more than one week. The non-pertechnetate species is also slightly air sensitive and is slowly oxidized to TcO₄⁻.²⁷

These results allow the assignment of XANES spectra of the non-pertechnetate species shown in Fig. 1 to a Tc(I) carbonyl complex, either a *fac*-Tc(CO)₃ or a Tc(CO)₂(NO) complex. Consequently, the non-pertechnetate species is most likely a Tc(I) carbonyl complex, but given the similarity of the XANES spectra of these complexes, a definitive assignment of these spectra to a single Tc(I) carbonyl complex

based solely on XANES spectra is not possible. The ^{99}Tc -NMR data show that gluconate forms the most stable Tc(I) carbonyl complex of the ligands believed to be present in CC waste. However, depending upon the composition of the CC waste other complexes could exist. In any case, the chemistry of the non-pertechnetate species would be similar to that of $fac\text{-Tc}(\text{CO})_3(\text{gluconate})^{2-}$ although the charge may be different.

The observation of Tc(I) carbonyl species in high-level waste tanks at Hanford is surprising. However, gas in the head space of these tanks contains 0.25 to 0.5 mol % CO ,²⁸ presumably from decomposition of the organic compounds, and $fac\text{-Tc}(\text{CO})_3^+$ can be formed by reduction of pertechnetate at low CO concentrations.¹⁸ The putative identity of the non-pertechnetate species partially explains its resistance to oxidation: although Tc(I) carbonyl complexes are not thermodynamically stable in alkaline solution, they are kinetically inert due to their low-spin d^6 electronic configuration. This identification of the non-pertechnetate species will allow the development of strategies to remove it, strategies that will be quite different from those needed to remove pertechnetate.

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SUPPORTING INFORMATION PARAGRAPH: ^{99}Tc -NMR spectra of $fac\text{-Tc}(\text{CO})_3^+$ complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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