

Extraction of Pertechnetate and Perrhenate from Water with Deep-Cavity [CpFe(arene)]⁺-Derivatized Cyclotrimeratrylenes

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Technetium-99 (β^- , $t_{1/2} = 2.15 \times 10^5$ years) is produced in a 6% fission yield from fission reactors. Technetium-99 continues to be of major concern at various nuclear sites because of its mobility in its most common chemical form during the reprocessing cycle and in the environment. Under these oxic aqueous environments the chemical form of Tc is typically Tc(VII)O_4^- , which is difficult to remove. Methods for pertechnetate removal to date have mixed results and pose further environmental concerns. Utilization of new cyclotrimeratrylene host materials for the extraction of pertechnetate from 0.9% saline into nitromethane has shown high selectivity and efficiency. A deep-cavity host, tris[cyclopentadienyliron(II) arene]cyclotrimeratrylene (**2**), has shown >95% extraction of pertechnetate and perrhenate into nitromethane from saline in the presence of competing anions, outperforming previously reported materials.

Introduction

Anion recognition plays an important role in natural chemical processes. Among the evidence supporting this is that the large majority of characterized enzymes are anion binding.¹ X-ray crystal structures and NMR determinations of anion-binding proteins^{2–5} have shown that anion discrimination often results from complex hydrogen-bonding interactions combined with a size-exclusion fit process.

The development of simple anion host–guest chemistry has not been extensive due to difficulty in synthesizing proper hosts. The size, shape, and solvation energies of anions increase the number of requirements governing the geometry of a host. While much of supramolecular anion chemistry tries to emulate biological interactions, nonnatural receptor systems are proving to be of great interest in such applications as anion transport, catalysis, sensing, and environmental remediation.⁶

Technetium-99 (⁹⁹Tc) is a radionuclide produced in 6% yield from the thermal neutron fission of uranium and plutonium. This makes it one of the largest components of

nuclear waste material; each nuclear facility will produce approximately 40 kg of ⁹⁹Tc every year.⁷ In addition, its long half-life (2.15×10^5 years) poses a concern when considering long-term storage and environmental contamination from ballistics testing, fallout, and spent fuel reprocessing.

In aqueous solutions, ⁹⁹Tc is present in its heptavalent state as pertechnetate, $^{99}\text{TcO}_4^-$. This oxoanion is highly soluble and mobile in water, making it a potential environmental contaminant.⁸ Pertechnetate has a relatively fast clearance rate from the body, as shown from in vivo nuclear medicine use of $^{99\text{m}}\text{TcO}_4^-$.⁹ Some plants, and subsequently animals, have been shown to take up ⁹⁹Tc, metabolize and incorporate it, and then receive a radiation dose.^{10–12}

The problem of ⁹⁹Tc in the environment is not new. Methods for removing $^{99}\text{TcO}_4^-$ from aqueous media that have been reported are primarily based on solvent extraction and ion exchange.^{13–16} Previous methods have used tributyl

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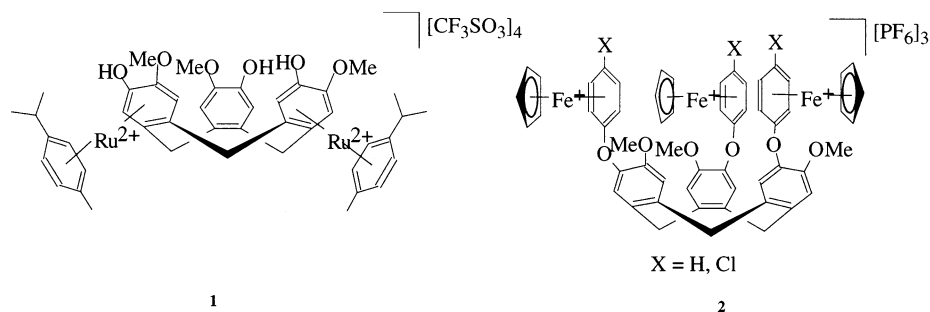


Figure 1. Structures of host materials: (1) bisruthenated cyclotrimeratrylene; (2) extended-cavity cyclotrimeratrylene.

phosphate,¹⁷ an extractant, and ion-pairing agents such as tetraorganoammonium, -phosphonium, and -arsonium salts,^{18,19} Primene JMT,²⁰ and triphenyltetrazolium chloride,²¹ utilizing extracting solvents such as chloroform, heptane, and toluene, with varying degrees of success. Unfortunately most of the solvents used in extractions are environmentally unsafe, posing an additional disposal issue, and the ion-pairing salts are not selective for pertechnetate. Methods using adsorption and ion exchange have also resulted in mixed success.^{22–27}

As environmental remediation and nuclear waste treatment issues increase, methods for cleanup and disposal and the eventual fate of subsequent waste generated must be carefully scrutinized for safety and efficiency. Methods are needed to remove ⁹⁹Tc without generating a larger volume of waste.²⁸ In the case of liquid–liquid extraction, it may be possible to recover the organic phase if a precipitation or back-extraction of ⁹⁹Tc into water is utilized. The selective removal of ⁹⁹TcO₄[−] in the presence of other anions is important to the cleanup of radioactive waste.

Recently we reported the development of a macrocycle based on a metalated cyclotrimeratrylene (**1**) host specifically designed to complex a TcO₄[−] guest (Figure 1).^{29,30} Extraction studies using a biphasic system composed of nitromethane and 0.9% aqueous saline showed this material to be promis-

ing in selectively extracting ⁹⁹TcO₄[−] (even over ReO₄[−]) from aqueous media.^{29,31} Two-phase (nitromethane/saline) anion-transport experiments were carried out to determine the degree of TcO₄[−] and ReO₄[−] complexation with **1** both alone and in competition with other anions. Greater than 90% of host **1** remained in the organic phase and acted as a phase-transfer agent for anions being extracted from the aqueous phase. Host **1** had a definite extraction selectivity for large tetrahedral oxoanions in the sequence TcO₄[−] ≥ ReO₄[−] > ClO₄[−] ≫ NO₃[−] > SO₄^{2−} > Cl[−].^{31,32} More recently, a host based on a similar macrocyclic arene trimer containing an extended cavity and metalated upper rim (**2**) was developed (Figure 1).³³ The selectivity and efficiency of this new host for binding TcO₄[−] in solution are reported.

Experimental Section

Materials. *Caution!* ⁹⁹Tc emits a low-energy (0.292 MeV) β[−] with a half-life of 2.15 × 10⁵ years. Although common laboratory glassware provides adequate shielding, standard radiation safety procedures must be used at all times. ^{99m}Tc emits a 140 keV γ-ray with a half-life of 6.0 h, and ¹⁸⁸Re emits a 155 keV γ-ray and a 2.1 MeV β[−]_{max} particle with a half-life of 17 h. These materials should be handled only in a controlled environment by qualified personnel trained in radiation safety.

The extended-cavity cyclotrimeratrylene **2** and [CpFe^{II}(benzene)]-BF₄ were prepared according to published literature procedures.^{33,34} Nitromethane (ACS grade), sodium phosphate, sodium nitrate, sodium sulfate, and sodium perchlorate were used as received. The ⁹⁹Tc was obtained from Oak Ridge National Laboratory as ammonium pertechnetate. Potassium pertechnetate was prepared by cation metathesis with KOH and subsequent concentration and precipitation. Ammonium perrhenate was used, as received, as a surrogate for pertechnetate-99 whenever possible. ^{99m}Tc was eluted with saline as sodium pertechnetate from a ⁹⁹Mo/^{99m}Tc generator (Mallinckrodt, St. Louis, MO). ¹⁸⁸Re was eluted with saline as sodium perrhenate from a ¹⁸⁸W/¹⁸⁸Re generator obtained from the Missouri University Research Reactor (MURR).

Instrumental Details. A NaI(Tl) solid scintillation well detector with Ortec electronics was used for counting γ-emitting samples. Windows were set for counting the radioisotope of interest. Experiments using more than one γ-emitting radionuclide were

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assayed with a Ge(Li) semiconductor detector with Canberra electronics and Maestro multichannel analysis software (EG&G Ortec, Inc.). Energy and efficiency calibrations were based on a ^{152}Eu source.

General Extraction Procedure. The aqueous phase (0.5 mL of 0.9% saline) containing various anions and 3 mM ReO_4^- or $^{99}\text{TcO}_4^-$ was extracted with a nitromethane phase (0.5 mL) containing the host by vortexing for 30 s followed by centrifugation to separate the phases. Aliquots (100 μL) of each phase were removed and counted for radioactivity using a NaI(Tl) well detector or a Ge(Li) semiconductor detector.

Oxoanion Competition Studies by Liquid–Liquid Extraction. A 3 mM nitromethane solution of **2** ($X = \text{H}$) and a 9 mM nitromethane solution of $[\text{CpFe}^{\text{II}}(\text{benzene})]\text{BF}_4$ were extracted according to the general procedure with an aqueous phase containing competing oxoanions (NaNO_3 , Na_2SO_4 , Na_3PO_4 , or NaClO_4) at a 3 mM concentration with $^{99m}\text{TcO}_4^-$ tracer in 0.9% w/v NaCl (saline).

Effect of pH. The general procedure with **2** was repeated with the aqueous phase at pH 4, 7, and 10 using 3 mM phosphate.

Effect of the MO_4^- : Host Mole Ratio. A 0.9% w/v saline aqueous phase (0.5 mL) containing 3 mM competing oxoanions (NaNO_3 , Na_2SO_4 , Na_2HPO_4 , or NaClO_4) was extracted with a 3 mM nitromethane solution of **2** (0.5 mL). The ReO_4^- concentration in the aqueous phase was varied from 3 to 0.15 mM and was spiked with both $^{99m}\text{TcO}_4^-$ and $^{188}\text{ReO}_4^-$.

Comparison of Perrhenate and Pertechnetate. The mole ratio experiment was repeated using 3 mM solutions of either ReO_4^- or $^{99}\text{TcO}_4^-$ as the bulk solution, with each carrier being spiked individually with $^{99m}\text{TcO}_4^-$ and $^{188}\text{ReO}_4^-$ as the radiotracer. Aliquots (100 μL) of each phase were counted for radioactivity using a NaI(Tl) well detector and a Ge(Li) semiconductor detector.

Results and Discussion

The extended-cavity cyclotrimeratrylene analogue **2** (Figure 1) was investigated as a host for selective binding of pertechnetate in the presence of a variety of competing anions, and was found to be an excellent material for extracting pertechnetate from aqueous environments.

Oxoanion Competition Studies by Liquid–Liquid Extraction. One of the important criteria for pertechnetate removal is high selectivity. This can be tested by competition studies with NO_3^- , SO_4^{2-} , and PO_4^{3-} because of their high abundance in natural waters and/or nuclear fuel reprocessing streams and ClO_4^- as a positive control because of its suppression of ReO_4^- binding with **1**.^{29,32} The data in Figure 2 indicate that **2** removes $^{99m}\text{TcO}_4^-$ selectively and efficiently from water in competition with NaNO_3 , Na_2SO_4 , Na_3PO_4 , or NaClO_4 . This phenomenon could easily be attributed to simple ion pairing rather than a cavity-binding host–guest relationship. A primary control experiment is also presented in Table 1 with a noncavity pendant $[\text{Cp}(\text{Fe}^{\text{II}}(\text{benzene}))]$ control, which can potentially act as a nonspecific ion-pairing agent. Because the noncavity control has only one Fe center and an overall +1 charge, the concentration used was 3 times that of **2** to give the same charge distribution in the nitromethane phase. Comparison of the results (Table 1) suggests that the guest binds within the cavity of **2**. The control extracted $25 \pm 12\%$ of the pertechnetate (nanomolar concentration) in the presence of NO_3^- , SO_4^{2-} , and PO_4^{3-}

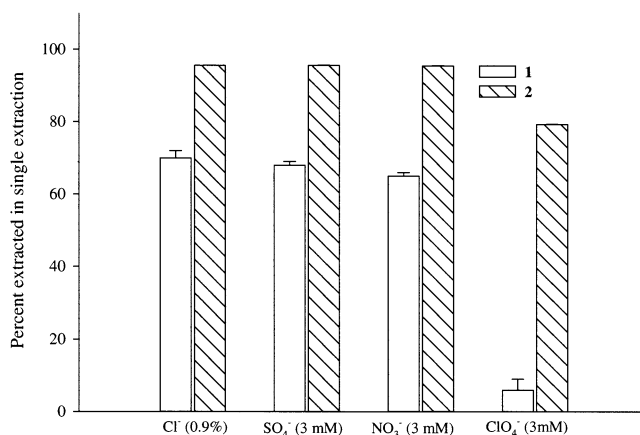


Figure 2. Comparison of extraction efficiency between **1** and **2**. Host, guest, and competing anion concentrations are 3 mM.

Table 1. Comparison of the Extraction Efficiency of **2** and Noncavity Pendant $\text{CpFe}^{\text{II}}(\text{benzene})^a$

competing anion	3 mM 2	9 mM $\text{CpFe}^{\text{II}}(\text{benzene})$
SO_4^{2-}	97.2 ± 0.4	27.2 ± 14.8
ClO_4^-	78.9 ± 0.6	2.7 ± 0.8
HPO_4^-	96.8 ± 0.5	25.6 ± 14.0
NO_3^-	95.5 ± 0.1	21.0 ± 9.7

^a The concentrations of **2** and ReO_4^- are 3 mM, and the concentration of $\text{CpFe}^{\text{II}}(\text{benzene})$ is 9 mM.

and $2.7 \pm 0.8\%$ in the presence of ClO_4^- . In contrast, **2** extracted $79 \pm 0.1\%$ of the pertechnetate in the presence of perchlorate and $95 \pm 0.1\%$ in the presence of the others. Studies comparing **1** and **2** as the host showed a significant increase in extraction efficiency of **2** (Figure 2). The comparable shallow-cavity metalated arene **1** did not extract pertechnetate as well as **2**. While the 20% increase in efficiency of **2** over **1** in the presence of the common “natural” anions is substantial, the increase of over 70% extraction efficiency in the presence of perchlorate is very significant, indicating that **2** has a very high selectivity for pertechnetate. Back-extraction with 0.9% saline has shown only 3% extraction of traced perrhenate back into the new saline, indicating that the perrhenate ions remain associated with the host.

Effect of pH. The effect of pH on the extraction of pertechnetate by the host is of importance because large variations in pH may be encountered. For example, post-treatment fuel materials will have a very low pH,²⁷ while groundwater typically has a higher pH.^{22,23,27} Figure 3 shows that, at high and neutral pH, the extraction efficiency does not change significantly. At lower pH the efficiency drops slightly. This decrease in extraction at lower pH is consistent with results from other extraction methods (such as ion pairing).^{17–20}

Effect of the MO_4^- : Host Mole Ratio. The relative concentrations of host and MO_4^- were varied to determine (1) the mole ratio at which the extraction efficiency becomes saturated (no longer increases significantly) and (2) whether there are effects of competition as the target guest concentration is lowered. The effects of dilution of the ReO_4^- on extraction efficiency were investigated by varying the host: guest ratio. Figure 4 shows the extraction results for

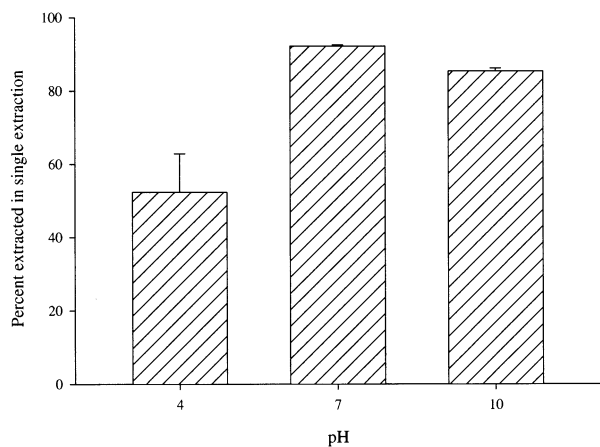


Figure 3. Effect of pH on extraction efficiency. **2** and bulk ReO_4^- concentrations are 3 mM.

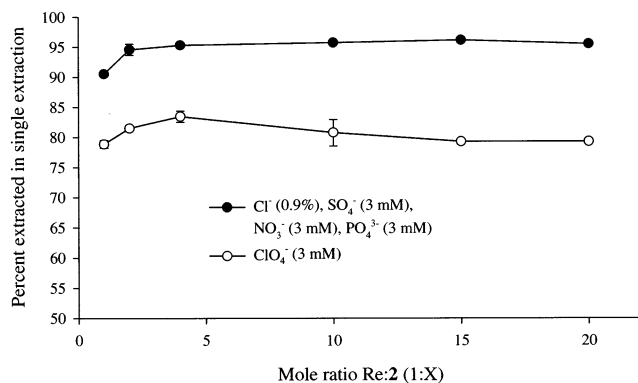


Figure 4. Extraction efficiency with varying guest concentrations. The host concentration is 3 mM. All anion data except those for perchlorate are shown together as they are not significantly different (paired t , $p < 0.998$, $n = 3$).

perrhenate as the mole ratio of **2** to Re was varied. The perrhenate concentration was continuously lowered, while the host concentration was maintained at 3 mM. The amount of perrhenate extracted in the presence of NO_3^- , SO_4^{2-} , and PO_4^{3-} increases slightly as the mole ratio of **2** to ReO_4^- approached 4:1 and then leveled off at approximately 95%. The behavior in the presence of ClO_4^- was similar, but at a lower binding efficiency (83%) as seen in the previous experiments. When the perrhenate concentration was held constant and the host concentration was varied, the trend was similar.

Comparison of Perrhenate and Pertechnetate. Although perrhenate is typically considered to be a nonradioactive chemical analogue for pertechnetate, a comparison between them must be performed to show the chemical equivalencies of the congeners. Studies in which $^{99}\text{TcO}_4^-$ was the carrier rather than ReO_4^- show that **2** extracts $^{99\text{m}}\text{TcO}_4^-$ equivalently regardless of the carrier anion (Figure 5). They also show that the ^{188}Re tracer had significantly, though not substantially, higher extractions when $^{99}\text{TcO}_4^-$ was the carrier. This suggests that **2** has a higher selectivity for pertechnetate

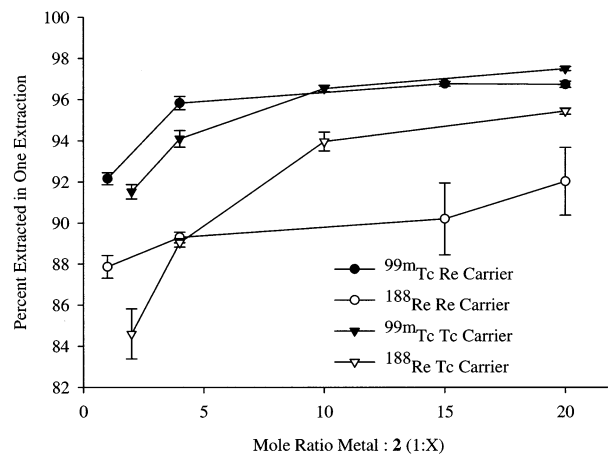


Figure 5. Comparison of TcO_4^- and ReO_4^- when extracted by **2**. The host concentration is 3 mM.

relative to perrhenate. This trend of higher selectivity for $^{99}\text{TcO}_4^-$ over ReO_4^- is similar to that seen in our previous studies with **1**, though at higher percent extraction and lower differentiation.^{29,32}

We have previously shown that metalation of cyclic arenes is useful for the extraction of metal anions.^{29–31} The first-generation host utilized in the extraction of pertechnetate also showed that this type of host can be selective for tetrahedral oxoanions.^{29,30} This led to the synthesis of a second generation of host material (**2**) that not only maintains the selectivity of the first generation, but is also more efficient. Because of similarities between the two generations of host materials in solution studies and the use of noncavity control studies, we can conclude that pertechnetate resides within the cavity when initially bound to the host.^{29,30}

Conclusions

We have shown that macrocycle hosts can be modified for selectivity toward pertechnetate. The driving force for this host–guest interaction apparently results from a good fit of a combination of charge, size, and shape interactions between the host and pertechnetate. ^{99}Tc continues to be one of the major concerns of the U.S. Department of Energy in the cleanup of its sites and the migration of radioactive materials from these sites.^{35,36} This new material has high efficiency in selectively extracting pertechnetate, although modification will be necessary to allow it to be soluble in more environmentally safe solvents. The ability to create designer extractant materials can be a great asset to environmental abatement problems.

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