

Reduction of Pertechnetate by Acetohydroxamic Acid: Formation of  $[\text{Tc}^{\text{II}}(\text{NO})(\text{AHA})_2(\text{H}_2\text{O})]^+$  and Implications for the UREX ProcessCynthia-May S. Gong,<sup>†</sup> Wayne W. Lukens,<sup>‡</sup> Frederic Poineau,<sup>†</sup> and Kenneth R. Czerwinski<sup>\*†</sup>

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Reductive nitrosylation and complexation of ammonium pertechnetate by acetohydroxamic acid has been achieved in aqueous nitric and perchloric acid solutions. The kinetics of the reaction depend on the relative concentrations of the reaction components and are accelerated at higher temperatures. The reaction does not occur unless conditions are acidic. Analysis of the X-ray absorption fine structure spectroscopic data is consistent with a pseudo-octahedral geometry and the linear Tc–N–O bond typical of technetium nitrosyl compounds, and electron spin resonance spectroscopy is consistent with a  $d^5$  Tc(II) nitrosyl complex. The nitrosyl source is generally AHA, but it may be augmented by some products of the reaction with nitric acid. The resulting low-valency *trans*-aquaonitrosyl(diacetohydroxamic)-technetium(II) complex ( $[\text{Tc}^{\text{II}}(\text{NO})(\text{AHA})_2\text{H}_2\text{O}]^+$ , **1**) is highly soluble in water, extremely hydrophilic, and is not extracted by tri-*n*-butylphosphate in a dodecane diluent. Its extraction properties are not pH-dependent: potentiometric-spectrophotometric titration studies indicate a single species from pH 4 down to  $-0.6$  (calculated). This molecule is resistant to oxidation by  $\text{H}_2\text{O}_2$ , even at high pH, and can undergo substitution to form other technetium nitrosyl complexes. The potential formation of **1** during reprocessing may strongly impact the fate of technetium in the nuclear fuel cycle.

## Introduction

Technetium, a transition-metal radioelement, is a major fission product in spent nuclear fuel. Its fate in the UREX reprocessing scheme is modeled as pertechnetate ( $\text{TcO}_4^-$ ),<sup>1–3</sup> however, recent work has shown that soluble, low-valency complexes can form in waste-containing organic ligands.<sup>4</sup>

Acetohydroxamic acid (AHA) is an organic ligand proposed for use in the UREX process.<sup>5</sup> It reduces neptunium

and plutonium,<sup>6,7</sup> and the resultant hydrophilic complexes are separated from uranium by extraction with tributylphosphate (TBP) in a hydrocarbon diluent.<sup>8,9</sup> Hydroxamic acids undergo hydrolysis to hydroxylamine and the pertinent carboxylic acid.<sup>10</sup> The reported reduction potentials of AHA and pertechnetate<sup>6,7,11,12</sup> indicate that it may be possible for AHA to reduce technetium, altering its fate in the fuel cycle. However, as demonstrated for hydroxylamine,<sup>13</sup> in these systems the electrochemistry is largely controlled by other species, especially NO, adsorbed on the platinum electrode

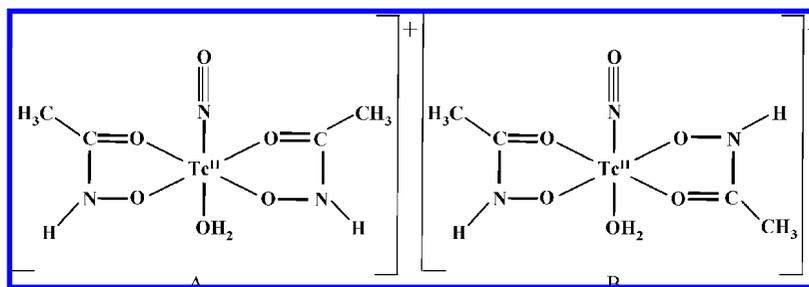
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- (1) Schroeder, N. C.; Attrep, M.; Marrero, T. *Technetium and Iodine Separations in the UREX Process; LA-UR-01-6607*; Los Alamos National Laboratory: Los Alamos, NM, 2001; 6–19.
- (2) Uchiyama, G.; Asakura, T.; Hotoju, S.; Mineo, H.; Kamei, K.; Watanabe, M.; Fujine, S. *Radiochem.* **2000**, *42*, 488–492.
- (3) Koltunov, V. S.; Marchenko, V. I.; Nikiforov, A. S.; Smelov, V. S.; Shmidt, V. S.; Gomonova, T. V.; Polunin, A. K.; Kondra'ev, B. A. *Atomnaya Energiya (trans.)* **1986**, *60*, 35–41.
- (4) Lukens, W. W.; Shuh, D. K.; Schroeder, N. C.; Ashley, K. R. *Environ. Sci. Technol.* **2004**, *38*, 229–233.
- (5) Taylor, R. J.; May, I.; Wallwork, A. L.; Denniss, I. S.; Hill, N. J.; Galkin, B. Ya.; Zilberman, B. Ya.; Federov, Yu. S. *J. Alloys Compd.* **1998**, *271–273*, 534–537.

- (6) Taylor, R. J.; May, I. *Czech. J. Phys.* **1999**, *49*, S1 617–621.
- (7) Chung, D. Y.; Lee, E. H. *Bull. Korean Chem. Soc.* **2005**, *26*, 1692–1694.
- (8) May, I.; Taylor, R. J.; Brown, G. *J. Alloys Compd.* **1998**, *271–273*, 650–653.
- (9) May, I.; Taylor, R. J.; Denniss, I. A.; Brown, G.; Wallwork, A. L.; Hill, N. J.; Rawson, J. M.; Less, R. *J. Alloys Compd.* **1998**, *275–277*, 769–772.
- (10) Chung, D. Y.; Lee, E. H. *J. Ind. Eng. Chem.* **2006**, *12*, 962–966.
- (11) Schwochau, K. *Technetium: Chemistry and Radiopharmaceutical Applications*; Wiley-VCH: Weinheim, 2000; Chapter 6.
- (12) Cinquantini, A.; Zanello, P.; Mazzocchin, G. A. *J. Electroanal. Chem.* **1977**, *80*, 387–393.
- (13) Rosca, V.; Beltramo, G. L.; Koper, M. T. M. *J. Electroanal. Chem.* **2004**, *566*, 53–62.



**Figure 1.** A, *trans*-aquonitrosyl-*cis*-diacetohydroxamic-technetium(II); B, *trans*-aquonitrosyl-*trans*-diacetohydroxamic-technetium(II).

surface, and the reported reduction potentials for AHA may not be accurate. The detailed mechanism for oxidation of AHA in solution has not been reported; however, in the gas-phase, AHA is oxidized by a single electron to  $\text{AHA}^+$ , which quickly decomposes to acetyl cation and aminoxyl radical ( $\text{H}_2\text{NO}^*$ ).<sup>14</sup> In solution, AHA may be oxidized by a single electron, yielding  $\text{AHA}^+$ , which is then hydrolyzed to yield acetic acid and aminoxyl radical, which quickly disproportionates to  $\text{N}_2$  and water. The electrochemistry of AHA as well as its reaction chemistry may be complicated by the fact that aminoxyl radical is itself a good reducing agent, yielding nitroxyl (HNO) upon oxidation.<sup>15</sup> Previous studies of the behavior of technetium during the UREX process have not reported a reduction,<sup>1</sup> but AHA is known to react immediately with Ru(III) in aqueous solution to yield a Ru(II) nitrosyl complex.<sup>16</sup>

More research has been performed on the interaction of hydroxylamine, also a reductant, and pertechnetate. In aqueous HCl, hydroxylamine can reduce Tc(VII) to form Tc(IV) hydroxylamine and chloride complexes.<sup>17,18</sup> Reaction of technetium with hydroxylamine often gives a mixture of products, most notably Eakins' pink complex<sup>19</sup> (2,  $[\text{Tc}^{\text{I}}(\text{NO})(\text{NH}_3)_4]\text{Cl}_2$ ), the first reported technetium nitrosyl (TcNO) complex. The source of NO may be hydroxylamine or its oxidation products,  $\text{H}_2\text{NO}$ , or  $\text{HNO}$ .<sup>20</sup> Since its synthesis in 1963, reports on its chemistry<sup>21</sup> and crystal structure<sup>22</sup> have launched the production of an expanding number of technetium nitrosyl compounds, often by substitution,<sup>23–29</sup> but also synthesized directly from Tc(IV) halides

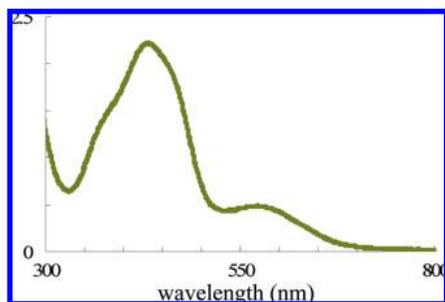
using hydroxylamine,  $\text{NaNO}_2$ ,  $\text{NO}(\text{g})$ , or NO salts as the sources of nitrosyl.<sup>19,30</sup> Only recently have researchers exploited reductive nitrosylation of pertechnetate by hydroxylamine as a route to technetium nitrosyl complexes.<sup>31</sup>

The strong  $\pi$ -acceptor character of the nitrosyl ligand stabilizes low-valent technetium through backbonding, and few Tc(II) complexes without nitrosyl or thionitrosyl ligands are known.<sup>32,33</sup> Most technetium nitrosyl complexes are pseudo-octahedral Tc(I) and Tc(II) complexes and trigonal bipyramidal Tc(III) complexes.<sup>34–36</sup> The strong  $\pi$ -acidity of nitrosyl decreases the lability of the other ligands. Given the strong hydrophilicity of known AHA complexes, this stability may affect the fate of technetium in the fuel cycle and the strategies necessary to create a final waste form.

In this work, it is demonstrated that pertechnetate undergoes reductive nitrosylation by AHA under a variety of conditions. The resulting divalent technetium is complexed by AHA to form the pseudo-octahedral *trans*-aquonitrosyl-(diacetohydroxamic)-technetium(II) complex ( $[\text{Tc}^{\text{II}}(\text{NO})(\text{AHA})_2\text{H}_2\text{O}]^+$ ) (1, Figure 1), as characterized by extended X-ray absorption fine structure spectroscopy (EXAFS) – the first EXAFS reported for a technetium nitrosyl complex. This complex is the sole technetium product of the reaction and is different from the product of reaction of pertechnetate with the AHA hydrolysis products hydroxylamine and acetic acid. The observed partial orders of the reagents were determined and a potential mechanism proposed. In contrast to AHA complexes of other divalent transition metals,<sup>37–39</sup> divalent uranyl,<sup>40</sup> and Cr(V),<sup>41</sup> 1 is very soluble in water and stable

- (14) Jobst, K. J.; Burgers, P. C.; Ruttink, P. J. A.; Terlouw, J. K. *Int. J. Mass. Spect.* **2006**, *254*, 127–135.  
 (15) Lind, J.; Merényi, G. *J. Phys. Chem. A* **2006**, *110*, 192–197.  
 (16) Marmion, C. J.; Murphy, T.; Docherty, J. R.; Nolan, K. B. *Chem. Commun.* **2000**, 1153–1154.  
 (17) Taylor, R. J.; May, I. *Sep. Sci. Technol.* **2001**, *36*, 1225–1240.  
 (18) Koltunov, V. S.; Taylor, R. J.; Gomonoova, T. V.; Denniss, I. S. *Radiochim. Acta* **1997**, *76*, 71–76.  
 (19) Eakins, J. D.; Humphreys, D. G.; Mellish, C. E. *J. Chem. Soc.* **1963**, 6012–6016.  
 (20) Dutton, A. S.; Fukuto, J. M.; Houk, K. N. *Inorg. Chem.* **2005**, *44*, 7687–7688.  
 (21) Armstrong, R. A.; Taube, H. *Inorg. Chem.* **1976**, *15*, 1904–1909.  
 (22) Radonovich, L. J.; Hoard, J. L. *J. Phys. Chem.* **1984**, *88*, 6711–6716.  
 (23) Nicholson, T.; Hirsch-Kuchma, M.; Freiberg, E.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1998**, *279*, 206–209.  
 (24) Nicholson, T.; Hirsch-Kuchma, M.; Shellenbarger-Jones, A.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1998**, *267*, 319–322.  
 (25) Blanchard, S. S.; Nicholson, T.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1997**, *254*, 225–231.  
 (26) Blanchard, S. S.; Nicholson, T.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *241*, 95–100.  
 (27) Roseberry, A. M.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1990**, *176*, 179–181.

- (28) Abram, U.; Kirmse, R.; Köhler, K.; Lorenz, B.; Kaden, L. *Inorg. Chim. Acta* **1987**, *129*, 15–20.  
 (29) Linder, K. E.; Davison, A.; Dewan, J. C.; Costello, C. E.; Maleknia, S. *Inorg. Chem.* **1986**, *25*, 2085–2089.  
 (30) Schibli, R.; Marti, N.; Maurer, P.; Spingler, B.; Lehaire, M.-L.; Gramlich, V.; Barnes, C. L. *Inorg. Chem.* **2005**, *44*, 683–690.  
 (31) Nicholson, T.; Müller, P.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **2006**, *359*, 1296–1298.  
 (32) Lu, J.; Clarke, M. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1243–1248.  
 (33) Barrera, J.; Burrell, A. K.; Bryan, J. C. *Inorg. Chem.* **1996**, *35*, 335–341.  
 (34) Raynor, J. B.; Kemp, T. J.; Thyer, A. M. *Inorg. Chim. Acta* **1992**, *193*, 191–196.  
 (35) Tisato, F.; Refosco, F.; Bandoli, G. *Coord. Chem. Rev.* **1994**, *135/136*, 325–397.  
 (36) de Vries, N.; Cook, J.; Davison, A.; Nicholson, T.; Jones, A. G. *Inorg. Chem.* **1990**, *29*, 1062–1064.  
 (37) Dominey, L. A.; Kustin, K. *Inorg. Chem.* **1984**, *23*, 103–108.  
 (38) Brown, D. A.; Glass, W. K.; McGardle, S. J. C. *Inorg. Chim. Acta* **1983**, *80*, 13–18.  
 (39) Rudzka, K.; Makowska-Grzyska, M. M.; Szajna, E.; Arif, A. M.; Berreau, L. M. *Chem. Commun.* **2005**, *4*, 489–491.  
 (40) Gong, C. S.; Poineau, F.; Czerwinski, K. R. *Radiochim. Acta* **2007**, *95*, 439–450.



**Figure 2.** Basis spectrum of **1**. Y axis, absorption  $\times 10^3$ .  $\lambda_{\text{max}} = 428$  nm,  $\epsilon = 2216$  L mol $^{-1}$  cm $^{-1}$ .

**Table 1.** Fitting Parameters<sup>a</sup>

neighbor	# of neighbors	distance (Å)	$\sigma^2$ (Å $^2$ )	F-test (p) <sup>b</sup>
N	1	1.77(1)	0.004(2)	$2 \times 10^{-3}$
O	5	2.06(1)	0.006(1)	$2 \times 10^{-8}$
O <sup>c</sup>	1	2.95(1)	0.003(1)	$5 \times 10^{-4}$

<sup>a</sup>  $S_0^2 = 1.13$  (from fitting the TcO $_4^-$  reference),  $\Delta E_0 = 0(2)$  eV. <sup>b</sup> The probability that improvement in the fit quality resulting from adding these atoms is due to chance. <sup>c</sup> Nitrosyl oxygen. Includes 2 multiple scattering (MS) paths with the same parameter.

for months in a 0.235 M solution. Like the plutonium and neptunium AHA complexes, **1** is extremely hydrophilic and does not extract into 30% TBP in dodecane, which could be exploited in nuclear fuel separation schemes. Its stability, solubility, and straightforward aqueous synthesis could allow its use as a precursor to other technetium nitrosyl complexes.

## Experimental Section

**Caution!** <sup>99</sup>Tc is a  $\beta$ -emitter ( $E_{\text{max}} = 294$  keV,  $t_{1/2} = 2 \times 10^5$  years). All operations were carried out in radiochemical laboratories equipped for handling this isotope.

**Reagents and Solutions.** Ammonium pertechnetate was purchased from Oak Ridge National Laboratory and purified as described elsewhere.<sup>42</sup> Water was purified to  $> 18$  M $\Omega$  by a MilliQ system. All other chemicals were used as received. A 0.18 M technetium stock solution was prepared for all studies, and its concentration was confirmed spectrophotometrically at 289 nm ( $\epsilon = 2380$  L mol $^{-1}$  cm $^{-1}$ ) and/or via liquid scintillation counting (LSC) for every experiment. Amorphous TcO $_2$  was generated by adding hydrazine hydrate to a solution of ammonium pertechnetate, then washing the resultant black precipitate twice with ultrapure water. Stock solutions of up to 5.0 M AHA and hydroxylamine hydrochloride were generated frequently and in small batches to avoid hydrolysis. For the organic phase (30% TBP), 30 mL of tributylphosphate were diluted up to 100 mL with *n*-dodecane.

**Analytical Techniques.** UV–vis spectra were obtained using Varian Cary 6000i and Ocean-Optics ST2000 spectrometers. Temperature was monitored and maintained via a Varian Peltier thermostable multicell sample holder. Liquid scintillation counting was performed on a PerkinElmer Tri-Carb 3100TR instrument.

Electron paramagnetic resonance (EPR) spectra were obtained at room temperature with a Varian E-12 spectrometer equipped with a cryostat cooled by liquid nitrogen boil-off, an EIP-547 microwave frequency counter, and a Varian E-500 gaussmeter, which was calibrated using 2,2-diphenyl-1-picrylhydrazyl (DPPH,  $g = 2.0036$ ). The low-temperature spectrum was fit using a version of the code

ABVG modified to use a pseudo Voigt line shape and modified to fit spectra using the downhill simplex method. The ABVG code includes second-order effects in the calculation of the peak positions but cannot simulate anisotropic line widths, so all peaks in the simulation have the same line width.<sup>43,44</sup> In the least-squares fit, the spectrum at fields less than 2400 G and greater than 3900 G was weighted 3 times more heavily than the spectrum between 2400 and 3900 G due to problems caused by the narrower peaks at the center of the spectrum. The simulated solution spectra were also calculated using a downhill simplex version of ABVG in which all  $g$  and  $A$  values were identical. For the solution spectra, the simulation used a Lorentzian line shape with the line width dependence described by Kivelson.<sup>44–46</sup>

X-ray absorption fine structure (XAFS) spectra were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) at beamline 11–2 using a Si(220) double crystal monochromator. All <sup>99</sup>Tc samples were triply contained inside sealed polyethylene vessels. Higher-order harmonics were rejected by detuning the monochromator by 30%. X-ray absorption spectra were obtained in the transmission mode at room temperature using argon-filled ionization chambers. The spectra were energy calibrated using the first inflection point of the pre-edge peak from the technetium K-edge spectrum of an aqueous solution of NH $_4$ TcO $_4$ , defined as 21044 eV. To determine the technetium K-edge charge-state shifts, the energies of the technetium K-edges at half-height were used. Extended X-ray absorption fine structure (EXAFS) data analysis was performed by standard procedures using the programs ifeffit<sup>47</sup> and Athena/Artemis;<sup>48</sup> theoretical EXAFS phases and amplitudes were calculated using FEFF7.<sup>49</sup> Fitting of the technetium K-edge spectrum of the reaction product of TcO $_4^-$  with AHA was performed as previously described.<sup>47</sup> Statistical relevance of the EXAFS parameters was checked using the F-test.<sup>50</sup>

**Generation of Technetium Compounds.** [Tc<sup>II</sup>(NO)(AHA) $_2$ -H $_2$ O] $^+$ , **1**. A typical 1 mL reaction was initiated by adding 10  $\mu$ L of a 180 mM NH $_4$ TcO $_4$  stock solution to 800  $\mu$ L 5 M AHA and 125.5  $\mu$ L H $_2$ O in a 1.5 mL cuvette. After mixing, 64.5  $\mu$ L 70% HNO $_3$  was added and the solutions mixed thoroughly, then followed by UV–vis spectroscopy. The reaction reached equilibrium after approximately 2 weeks with the solution controlled at 20  $^\circ$ C. Heating decreased the time to reach equilibrium. Although **1** could be detected in any solution exceeding 0.05 mM TcO $_4^-$ , 0.5 M H $^+$ , and 0.5 M AHA, maximum conversion of pertechnetate to nitrosyl was found at concentrations of 1 M HNO $_3$  or HClO $_4$  and 4 M AHA. Higher acid concentrations promoted AHA hydrolysis rather than technetium reduction.

The effects of acid, technetium, and AHA concentrations were determined by systematically varying the initial concentrations over a series of three or more values at constant temperature (Figures S1 and S2 of the Supporting Information). One milliliter solutions from 0.05 to 1 mM TcO $_4^-$  in up to 4.0 M AHA and up to 2.0 M HClO $_4$  or HNO $_3$  were generated by diluting the technetium stock

(41) Gez, S.; Luxenhofer, R.; Levina, A.; Codd, R.; Lay, P. A. *Inorg. Chem.* **2005**, *44*, 2934–2943.

(42) Kopunec, R.; Abudeab, F. N.; Makaiova, I. J. *Radioanal. Nucl. Chem.* **1996**, *208*, 207–228.

(43) Bruce, S. D.; Higinbotham, J.; Marshall, I.; Beswick, P. *H. J. Mag. Reson.* **2000**, *142*, 57–63.

(44) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in Fortran 77: The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, 1992.

(45) Daul, C.; Schläpfer, C. W.; Mohos, B.; Ammeter, J.; Gamp, E. *Comput. Phys. Commun.* **1981**, *21*, 385–395.

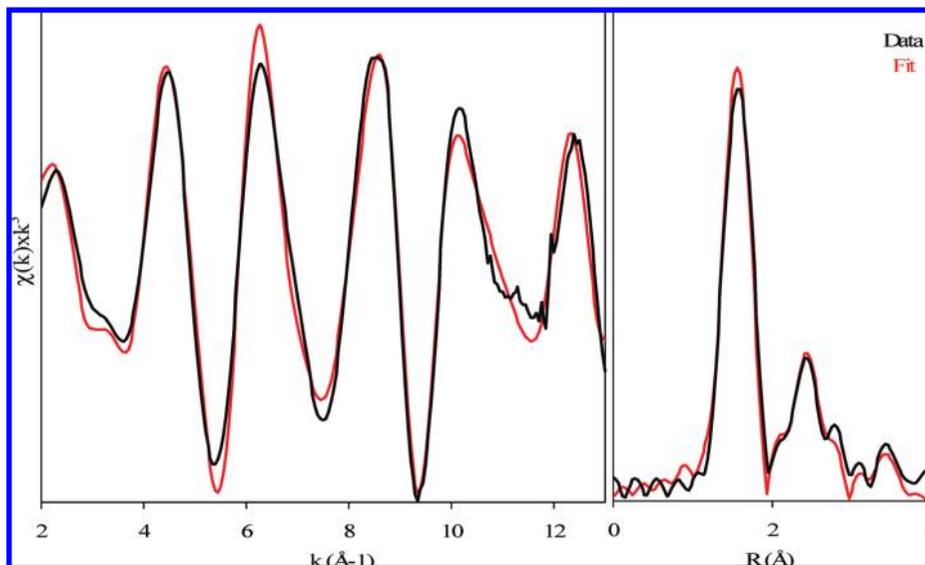
(46) Kivelson, D. J. *Chem. Phys.* **1960**, *33*, 1094–1106.

(47) Lukens, W. W.; Bücher, J. J.; Edelstein, N. M.; Shuh, D. K. *Environ. Sci. Technol.* **2002**, *36*, 1124–1129.

(48) Ravel, B.; Newville, M. *Phys. Scr.* **2005**, *T115*, 1007–1010.

(49) Rehr, J. J.; Albers, R. C.; Zabinsky, S. I. *Phys. Rev. Lett.* **1992**, *69*, 3397–3400.

(50) Downward, L.; Booth, C. H.; Lukens, W. W.; Bridges, F. *AIP Conference Proceedings* **2007**, *882*, 129–132.



**Figure 3.** Data (black lines) and fit (red lines) of the  $k^3$ -weighted EXAFS data and its Fourier transform.

**Table 2.** Comparison of **1** to Known TcNO Complexes

molecule	Tc–N (Å)	N–O (Å)	Tc–L <sub>trans</sub> (Å)	O–N–Tc
[Tc <sup>II</sup> (NO)(AHA) <sub>2</sub> (H <sub>2</sub> O)] <sup>+</sup> (this study)	1.77	1.18	2.06	180 °
Tc <sup>I</sup> (NO)(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> <sup>22</sup>	1.716(4)	1.203(6)	2.169(4)	178.7(2)°
Tc <sup>I</sup> Cl <sub>2</sub> NO(HNNC <sub>5</sub> H <sub>4</sub> N)(PPh <sub>3</sub> ) <sup>23</sup>	1.752(4)	1.1180(5)	2.153(4)	175.1(4)°
Tc <sup>I</sup> Cl <sub>2</sub> NO(py–PPh <sub>2</sub> –P,N)(PPh <sub>2</sub> –P) <sup>24</sup>	1.743(5)	1.170(6)	2.441(2)	177.2(5)°
Tc <sup>I</sup> NOBr <sub>2</sub> (CNCMe <sub>3</sub> ) <sub>2</sub> <sup>29</sup>	1.726(15)	1.136(17)	2.137(22)	174.9(8)°
[Tc <sup>I</sup> Cl(μ–Cl)(CO) <sub>2</sub> NO] <sub>2</sub> <sup>30</sup>	1.749(14)	1.16(2)	2.455(5)	177.4(8)°
[Tc <sup>I</sup> Cl(μ–Cl)(CO) <sub>2</sub> NO] <sub>2</sub> <sup>30</sup>	1.794(14)	1.15(2)	2.380(5)	174.3(9)°
[Tc <sup>I</sup> Cl(NO)(DPPE) <sub>2</sub> ]PF <sub>6</sub> ·CH <sub>2</sub> Cl <sub>2</sub> <sup>31</sup>	1.717(3)	1.145(3)	2.3262(7)	179.0(2)°
[Tc <sup>I</sup> NO(NH <sub>3</sub> )(phen) <sub>2</sub> ] <sub>2</sub> <sup>32</sup>	1.739(9)	1.160(9)		171.9(8)°
Tc <sup>III</sup> NOCl(SC <sub>10</sub> H <sub>13</sub> ) <sub>3</sub> <sup>36</sup>	1.767(6)	1.150(7)		175.9(2)°

solution into AHA, and then acidifying. All of the solutions turned from colorless to brown immediately upon the addition of acid, and the color deepened with time. Addition of acid early hydrolyzed the AHA before it reduced the pertechnetate.

The technetium concentration was confirmed for each sample by UV–vis and LSC in HClO<sub>4</sub> and by LSC in HNO<sub>3</sub>. The reactions were followed via UV–vis continuously for up to 12 days and intermittently up to 6 weeks (Figure S3 of the Supporting Information). The complex was also generated from amorphous TcO<sub>2</sub> dissolved to 0.235 M in a 4.0 M solution of AHA, and then acidified to 1 M H<sup>+</sup>. Dissolution of the anionic Tc(IV) complex [(*n*-Bu)<sub>4</sub>N]<sub>2</sub>[TcCl<sub>6</sub>] into 1.0 M AHA in dry ethanol did not generate any reaction over the period studied.

**Tc–Hydroxylamine.** A typical 1 mL reaction was initiated by adding 10 μL of a 180 mM NH<sub>4</sub>TcO<sub>4</sub> stock solution to 890 μL 4.5 M hydroxylamine HCl and 100 μL H<sub>2</sub>O in a 1.5 mL cuvette. The solutions were mixed thoroughly and then examined at regular time intervals by UV–vis spectroscopy. Both **2** and a yellow Tc–hydroxylamine (**3**) matching the description of Tc(IV) dihydroxylamine<sup>18</sup> were generated. The addition of nitric or perchloric acid was not necessary for this reaction, though it increased the rate. The effect of technetium, hydroxylamine, and additional acid concentrations on the formation of Tc–hydroxylamine compounds was monitored as above, from both pertechnetate and amorphous technetium dioxide, using hydroxylamine hydrochloride instead of AHA. The yellow **3** was purified from the pink **2** via extraction with 30% TBP.

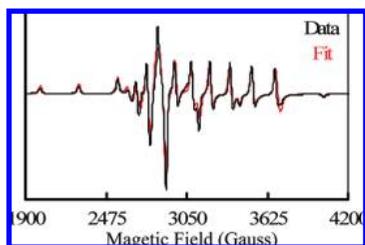
**Extraction.** The decrease in pertechnetate was followed by UV–vis and LSC in perchloric acid and by extraction with tetraphenylarsonium chloride in chloroform (TPACl)<sup>42</sup> and LSC in nitric acid. Extraction with 30% TBP was performed by combining equal volumes organic and aqueous phases and mixing

vigorously via vortexing for 60 s, followed by centrifugation. The technetium concentration in both phases was determined by LSC.

## Results and Discussion

**Generation and Characterization.** **1**, as confirmed by UV–vis spectrometry, was the only technetium species detected from the reaction of ammonium pertechnetate and AHA in acid. The reaction proceeded with concentrations as low as 0.5 M acid, 0.5 M AHA, and 0.05 mM NH<sub>4</sub>TcO<sub>4</sub>. [Tc<sup>II</sup>(NO)(AHA)<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup> can be generated consistently from ammonium pertechnetate at various temperatures: a sample generated by heating 20 mM NH<sub>4</sub>TcO<sub>4</sub>, 1 M HNO<sub>3</sub>, and 4 M AHA to 95 °C for 15 min, which visibly evolved gas, had the same UV–vis spectrum (Figure 2) as those generated from similar concentrations over 12 days at 20 °C and 4 days at 30 °C.

A sample that had reached equilibrium at pH 3.3 was divided: one portion was titrated with acid and the other with base. Spectra were taken at approximately half-integral pH values (Figure S4 of the Supporting Information). The concentration-corrected spectra were identical from pH –0.6 (calculated) up to pH 4, meaning that the kinetics could be tracked via the maximum at 428 nm, because, in contrast to the pH-sensitive spectrum of the uranium AHA complex,<sup>40</sup> **1** exhibits the same spectrum under all reaction conditions examined. Above pH 4, the spectrum began to shift, and the sample turned green in a basic environment. Addition of acid restored the original yellow-brown complex and its



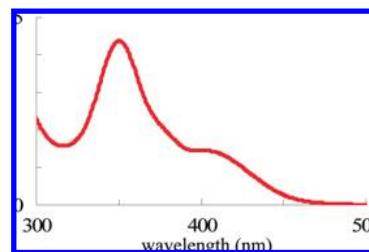
**Figure 4.** EPR spectrum of a frozen solution of **1**.

UV–vis spectrum immediately, indicating that the color change is due to deprotonation of the complex.

Because of radioactivity hazards, samples were microscale and contained only 5–100  $\mu\text{g}$  technetium each versus up to 120 mg nitrate or 200 mg perchlorate and up to 300 mg excess AHA and acetic acid. Attempts to isolate enough of the compound for IR and crystallographic studies via concentration, coprecipitation, ion exchange, extraction, and thin-layer chromatography were unsuccessful (Supporting Information). Therefore, the structure of **1** was studied by solution-phase EXAFS. The EXAFS fitting parameters are given in Table 1; fitted Fourier Transform and  $k^3$ -EXAFS spectra are shown in Figure 3. The geometry and bond lengths obtained by this method are consistent, within the error of the method, with those obtained by X-ray crystallography of known rhenium and technetium nitrosyl compounds (Table 2). The octahedral O,O bidentate bond has been similarly seen via EXAFS in iron,<sup>51</sup> and the M–N and N–O bond distances are consistent with those of rhenium(II) nitrosyl complexes.<sup>52</sup> It has been shown that AHA is an electron donor,<sup>9,53</sup> which may help stabilize the electron-withdrawing nitrosyl moiety.

The oxidation state of **1** was determined from its EPR spectrum, shown in Figure 4 in frozen solution and in Figure S5 (Supporting Information) in liquid solution. The  $g$  values  $g_1$ ,  $g_2$ , and  $g_3$ , obtained by fitting the spectrum shown in Figure 4 are 2.041, 2.028, and 1.949, respectively, and the associated hyperfine coupling constants  $A_{11}$ ,  $A_{22}$ , and  $A_{33}$ , are 118, 108, and  $259 \times 10^{-4} \text{ cm}^{-1}$ , respectively, with smaller, off-diagonal elements:  $A_{12}$ ,  $A_{13}$ , and  $A_{23}$  are 3, 33, and  $5 \times 10^{-4} \text{ cm}^{-1}$ , respectively. These  $g$  and  $A$  values are similar to those of Tc(II) nitrosyl complexes as reported in Table S1 of the Supporting Information. Of these complexes, the EPR parameters of **1** are most similar to those of trichloronitrosyl(acetylacetonato)–technetium, which is the only reported Tc(II) nitrosyl complex with an oxygen donor ligand that is similar to AHA. The spectroscopic data all support the proposed structure shown in Figure 1.

**Kinetics and proposed mechanism.** Unlike the reaction with AHA, the reaction of pertechnetate with hydroxylamine hydrochloride was not consistent. Occasionally, different aliquots of the same mother solution of the reagents generated different complexes, and in some cases, no reaction was observed. The solutions generally turned yellow over time, indicating the formation of **3**, but in some instances reaction



**Figure 5.** Basis spectrum of Tc(IV)–hydroxylamine. Y axis, absorption  $\times 10^3$ .  $\lambda_{\text{max}} = 350 \text{ nm}$ ,  $\epsilon = 4360 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

**Table 3.** Decrease in Pertechnetate; Total [Tc] 0.55 mM.

mol L <sup>-1</sup>	Rate ( $\Delta A_{289\text{nm}}/\text{min}$ )	
	hydroxylamine	AHA
3.66	–0.00020	–0.00170
1.83	–0.00010	–0.00020
0.92	–0.00004	–0.00003

produced **2**, confirmed by UV–vis comparison to literature, and even reversibly turned green upon heating (likely  $\text{TcNOCl}_5^{2-}$ ).<sup>54</sup> Both **2** and **3** formed more often in perchloric than in nitric acid. The UV–vis spectrum of **3** matches the description of a Tc(IV)–hydroxylamine complex, though its spectrum has not been published;<sup>18</sup> it is presented here in Figure 5. The rate of Tc(VII) reduction by hydroxylamine was much slower than that by AHA, as determined by UV–vis (Table 3).

Tc(IV) hexachloride,  $\text{TcCl}_6^{2-}$ , is often a starting material for synthesis of technetium nitrosyl complexes. This compound can be heated with hydroxylamine hydrochloride to form the tetra- and penta-chloronitrosyl Tc(II) complexes.<sup>55</sup> In this study, it was found that **1** can be formed from Tc(IV) as  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ . Dissolution of amorphous technetium dioxide into AHA forms a wine-red solution of a complex with a distinct UV–vis spectrum (**4**, Figure S6 of the Supporting Information), which upon acidification forms the yellow-brown **1**, reaching equilibrium within an hour at room temperature versus almost two weeks from pertechnetate. The initial red **4** could not be recovered even upon the addition of base (to 1.0 M) and hydrogen peroxide (to 1.0 M). The overall rate of the reductive nitrosylation of pertechnetate depends on the temperature, but by holding the temperature constant over a series of trials the partial order of each reagent in the production of **1** could be ascertained by observing the reaction over time (Tables 4, S2, and Figure S7 of the Supporting Information).

All of the complexes generated from hydroxylamine are distinct from  $[\text{Tc}^{\text{II}}(\text{NO})(\text{AHA})_2(\text{H}_2\text{O})]^+$ , indicating that the ligands on **1** are not formed from the acid hydrolysis of AHA to hydroxylamine and acetic acid. Attempts to form **1** from mixtures of hydroxylamine and acetic acid ligand in nitric and perchloric acids formed other distinct complexes whose UV–vis spectra varied with the ratio of hydroxylamine to acetic acid (Figure S8 of the Supporting Information). In contrast, the UV–vis spectrum of the reaction of AHA with pertechnetate was the same regardless of which mineral acid was used. These results strongly support the assignment of the equatorial ligands to AHA.

(51) Edwards, D. C.; Myneni, S. C. B. *J. Phys. Chem. A* **2006**, *110*, 11809–11818.

(52) Machura, B. *Coord. Chem. Rev.* **2005**, *249*, 2277–2307.

(53) Chatterjee, B. *Coord. Chem. Rev.* **1978**, *26*, 281–303.

**Table 4.** Partial Reaction Orders for the Reaction of  $\text{TcO}_4^-$  with AHA in Acid

Formation of Product, Monitored at 428 nm		
HNO <sub>3</sub>		
reagent	observed partial order	R <sup>2</sup>
NH <sub>4</sub> TcO <sub>4</sub>	1.028 ± 0.003	1.000
H <sup>+</sup>	0.991 ± 0.023	1.000
AHA	1.968 ± 0.149	0.994
HClO <sub>4</sub>		
reagent	observed partial order	R <sup>2</sup>
NH <sub>4</sub> TcO <sub>4</sub>	0.967 ± 0.003	1.00
H <sup>+</sup>	1.004 ± 0.037	0.999
AHA	1.994 ± 0.193	0.991
Loss of $\text{TcO}_4^-$ , monitored at 289 nm		
reagent	Observed Partial Order	R <sup>2</sup>
NH <sub>4</sub> TcO <sub>4</sub>	0.867 ± 0.055	0.996
HClO <sub>4</sub>	1.066 ± 0.052	0.998
AHA	1.742 ± 0.171	0.991

The slow rate of reaction of pertechnetate with AHA and the very rapid reaction of Tc(IV) with AHA, as well as the previously observed rapid reaction of Ru(III) with AHA, suggests that the technetium species reductively nitrosylated is a lower-valent complex. In addition, the nitrosylating agent must be AHA itself, because the rate of reductive nitrosylation of Tc(IV) is much faster than the rate of hydrolysis of AHA to hydroxylamine. Furthermore, the observation that Tc(IV) is much more reactive than Tc(VII) strongly supports a reductive nitrosylation mechanism similar to that previously proposed for the reductive nitrosylation of Ru(III), as illustrated in Scheme 1. The proposed mechanism is closely related to the previously proposed mechanism for reductive nitrosylation of V(V) by hydroxylamine studied by Wieghardt<sup>56</sup> and proceeds via a coordinated nitroxyl ligand previously observed.<sup>57</sup> Because the terminal oxo group of Tc(VI), Tc(V), or Tc(IV) is more nucleophilic than a terminal oxo group of  $\text{TcO}_4^-$ , the postulate that reductive nitrosylation proceeds by initial nucleophilic attack on the coordinated carbonyl group of AHA is consistent with the observed reactivity.

As the reaction of lower-valent technetium complexes with AHA is rapid, the initial step is most likely reduction of  $\text{TcO}_4^-$  to a lower-valent complex that subsequently undergoes reductive nitrosylation. The observed partial reaction orders provide two indications about the potential mechanism. First, steps prior to the rate determining step (rds) involve one  $\text{TcO}_4^-$ , one proton, and two molecules of AHA. Second, the rate law for formation of **1** is the same as that for loss of  $\text{TcO}_4^-$ ; therefore, all steps prior to the rds must be reversible. This latter fact eliminates the most straightforward mechanism for the reaction of  $\text{TcO}_4^-$  with AHA: the direct reaction of  $\text{TcO}_4^-$  with AHA to produce  $\text{TcO}_4^{2-}$ , which will rapidly disproportionate to Tc(V).<sup>58</sup> The reaction of  $\text{TcO}_4^-$  with AHA would be irreversible, yielding a rate law for loss of  $\text{TcO}_4^-$  equivalent to  $k[\text{TcO}_4^-][\text{AHA}]$ , not  $k[\text{TcO}_4^-][\text{H}^+][\text{AHA}]^2$ , as observed.

An alternative mechanism for reduction of  $\text{TcO}_4^-$  to Tc(VI) is suggested by the reaction of alkenes with Tc(VII) complexes.<sup>59</sup> In that study,  $\text{TcO}_4^-$  was unreactive, but an octahedral Tc(VII) complex,  $\text{TcO}_3(\text{AA})\text{Cl}_3$  where AA is a diamine ligand such as 1,10-phenanthroline, was sufficiently oxidizing to react with alkenes to form a coordinated diol ligand. Likewise,  $\text{TcO}_4^-$  may be insufficiently oxidizing to react with AHA, but an octahedral Tc(VII) complex is likely to be more oxidizing. The proposed mechanism for reduction of Tc(VII) to Tc(VI) involves a pre-equilibrium to form an octahedral Tc(VII) complex, as illustrated in Scheme 2. Thus, the overall proposed mechanism is the formation of an octahedral Tc(VII) complex that reacts with AHA to form an octahedral Tc(VI) complex, which either is reductively nitrosylated by the coordinated AHA ligand, as illustrated in Scheme 1, or disproportionates to form an octahedral Tc(V) complex that is reductively nitrosylated by the coordinated AHA ligand.

**Extraction.** In the absence of AHA, pertechnetate extraction into TBP was consistent with literature reports.<sup>60</sup> Pertechnetate reduction begins immediately upon contact with acidic AHA, as does the decrease in the extraction of technetium; the change in  $K_d$  with time is shown in Figure S9 of the Supporting Information. The increase of **1** from an initial solution of 0.5 mM  $\text{NH}_4\text{TcO}_4$  and 1 M  $\text{HNO}_3$ , charted as a function of AHA concentration via its absorbance maximum, can be correlated with a decrease of the technetium distribution between the aqueous and TBP phases. Figure 6 shows this relationship after the reaction has proceeded 24 h.

The reduction and complexation of technetium by AHA, even before complete transformation to the nitrosyl complex, inhibits its extraction into TBP. Even at 0.5 M AHA and 1.0 M  $\text{HNO}_3$  – conditions close to UREX+ – there is an immediate effect, culminating in a 42% reduction of the distribution constant after 1 day compared to the reaction without AHA. At 4.0 M AHA, only 1.4% of the technetium can be extracted after 1 day. When the reaction is allowed to proceed for just 4 h, then washed 5 times with TPACl to remove pertechnetate,<sup>42</sup> only 2% of the total technetium is extracted, similar to 1.5% for **2**, also a cationic technetium nitrosyl, and 2% for the red AHA **4** generated from Tc(IV) dioxide dissolved into a solution of AHA. This indicates that the species being extracted from the reaction mixture is simply unreacted pertechnetate. When chloride is substituted for the coordinated AHA by dilution of **1** into concentrated HCl (Figure S10 of the Supporting Information), the anionic chloronitrosyl technetium complex formed is extracted into TBP with a  $K_d$  of 0.92, very similar to the 0.95 of pertechnetate. These results indicate that it is not the nitrosyl moiety that affects the extraction of technetium; rather, it is the hydrophilicity of the AHA complex that inhibits the extraction of technetium. These complexes take time to form at 20 °C, but at the elevated temperatures likely encountered during reprocessing, their formation may be significantly faster.

Although the pH is changing, the distribution coefficient measured from pH –0.6 (calculated) up to 11 was the same

(54) Yang, G. C.; Heitzmann, M. W.; Ford, L. A.; Benson, W. R. *Inorg. Chem.* **1982**, *21*, 3242–3243.

(55) Brown, D. S.; Newman, J. L.; Thornback, J. R.; Pearlstein, R. M.; Davison, A.; Lawson, A. *Inorg. Chim. Acta* **1988**, *150*, 193–196.

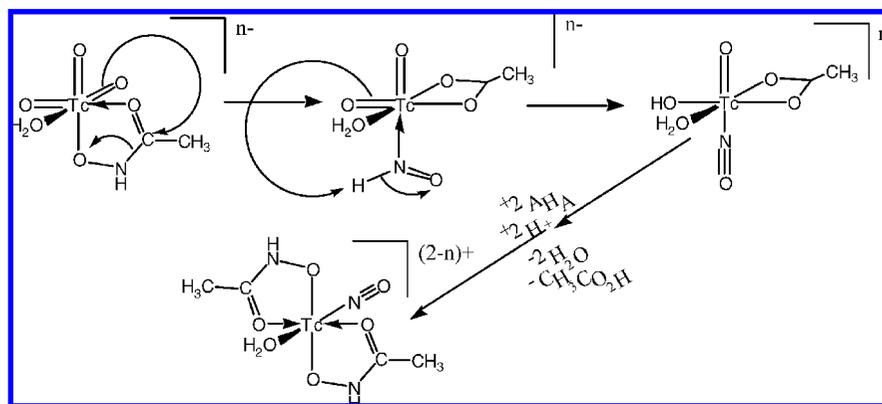
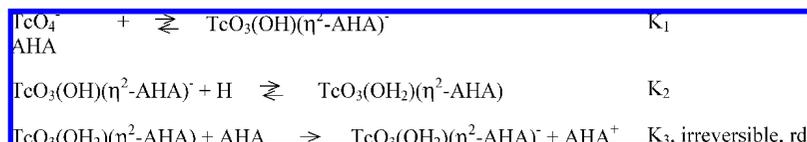
(56) Wieghardt, K.; Quilitzsch, U. *Z. Naturforsch.* **1981**, *36b*, 683–686.

(57) Southern, J. S.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 12406–12407.

(58) Founta, A.; Aikens, D. A.; Clark, H. M. *J. Electroanal. Chem.* **1987**, *219*, 221–246.

(59) Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *19/20*, 1981–1989.

(60) El-Kot, A. M. *J. Radioanal. Nucl. Chem.* **1992**, *163*, 363–373.

**Scheme 1.** Proposed Mechanism for Reductive Nitrosylation of Tc(VI) ( $n = 1$ ) or Tc(V) ( $n = 2$ ) by AHA**Scheme 2.** Proposed Mechanism for Reduction of  $\text{TcO}_4^-$  by AHA in Aqueous Acid

within error (Table S3 of the Supporting Information). The concentration of technetium in the organic phase was so low as to be immeasurable, and the difference in the concentration in the aqueous phase before and after extraction was within the error of the measurement: essentially no technetium is extracted into the organic phase. Conversely, **3** extracts into TBP, with a  $K_d$  of 1.35. The UV–vis spectrum in TBP is identical to that in aqueous solution, and extraction can be used to separate **3** from **2** after the reaction of pertechnetate with hydroxylamine.

## Conclusions

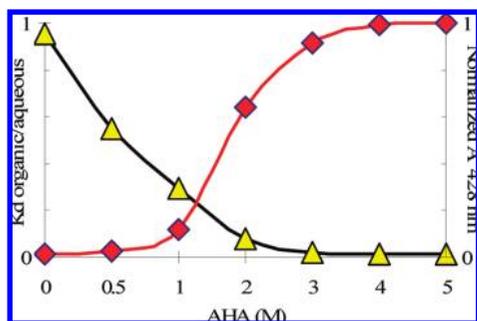
The Tc–nitrosyl structure determined by EXAFS is consistent with previously reported TcNO and metal–AHA structures. The facile formation of this complex from AHA without side products should advance interest in the synthesis of low-valency TcNO complexes directly from pertechnetate, especially if this reaction proceeds with other substituted hydroxamic acids.

The observation of pertechnetate reduction by AHA under conditions proposed for reprocessing, and its subsequent effect on the extraction behavior of technetium, is surprising and important. Currently, the UREX+ flow sheet indicates

that AHA is added to the dilute nitric acid scrub solution, which is loaded with uranium, technetium, neptunium, and plutonium, rather than the feed solution, which contains the spent fuel dissolved in concentrated nitric acid. With reduced concentrations of competing noble metal fission products, especially ruthenium, which easily forms nitrosyl complexes, conditions need to be assessed for the potential nitrosylation of technetium that results in the formation of inextractable technetium species, disrupting nuclear fuel separation schemes. Further studies are needed to determine whether the presence of actinides will affect the formation of these complexes, and thus the fate of technetium in the fuel cycle.

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**Supporting Information Available:** Description of attempts to purify the compound; tables showing the kinetics and comparison of EPR data with published values; figures showing the UV–vis spectra from pH titrations, kinetics of formation, kinetics of extraction, UV–vis characterization of Tc–hydroxylamine, Tc(IV)–AHA, and of competitive reactions with HCl. This material is available free of charge via the Internet at <http://pubs.acs.org>.

**Figure 6.** Correlation of absorbance of **1** at 428 nm with the distribution factor into 30% TBP–dodecane after 1 day. Triangles,  $K_d$ ; diamonds,  $A_{428\text{nm}}$ .

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