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Technetium Bis(μ-oxo) Dimers of 1,4,7-Triazacyclononane-N,N',N''-triacetate (TCTA). Synthesis and Characterization of $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{n-}$ (n = 2, 3) and the Crystal Structure of $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$

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The mixed-valence technetium(III/IV) bis(μ-oxo) dimer $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{3-}$ (**1**; TCTA = 1,4,7-triazacyclononane-N,N',N''-triacetate) has been prepared as its sodium and barium salts. This complex undergoes a reversible one-electron oxidation with potassium persulfate to form $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ (**2**). Both complexes have been characterized by elemental analysis, infrared, UV/visible, and resonance Raman spectroscopy, and fast atom bombardment mass spectrometry. A crystal structure analysis of the Tc(III/IV) dimer $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (**1c**) reveals that the two Tc atoms are linked by a planar $Tc(\mu\text{-}O)_2Tc$ ring. One TCTA ligand binds to each Tc through an N_3O donor set, and one of the acetate groups from each ligand bridges the two metal atoms. Crystal data for **1c** are a = 15.128 (1) Å, b = 18.822 (2) Å, c = 15.582 (1) Å, β = 105.43 (7)°, V = 4276.9 Å^3, space group $P2_1/n$, Z = 4, mol wt = 1366.8, ρ(calcd) = 2.122 g cm^{-3}, and μ = 23.9 cm^{-1}. Resonance Raman spectra of complexes **1** and **2** were obtained by irradiation at 514.5 nm; strong bands assigned to the four-membered $Tc(\mu\text{-}O)_2Tc$ ring and the metal-metal multiple bond were seen. The aqueous electrochemistry of the compounds confirms that they are related by a reversible one-electron wave. The Tc(III/IV) dimer **1** represents the first fully characterized Tc-(amino carboxylate) complex in an oxidation state lower than +4. Evidence for the existence of other Tc(III/IV) bis(μ-oxo) dimers of this type with amino carboxylate ligands such as EDTA and NTA is presented.

Introduction

The synthesis and crystal structure of the technetium(IV/IV) bis(μ-oxo) dimers $(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)$[1] and $K_2[(NTA)Tc(\mu\text{-}O)_2Tc(NTA)]$[2] (EDTA = ethylenediaminetetraacetate, NTA = nitrilotriacetate) have been reported. In this laboratory, we have found that the formation of bis(μ-oxo) dimers in the oxidation state Tc(IV) is a dominant theme in Tc-(amino carboxylate) chemistry and have prepared several new complexes that appear to be analogous to those reported previously. The synthesis of one of these new Tc(IV/IV) dimers, $Ba[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]$ (TCTA = 1,4,7-triazacyclononane-N,N',N''-triacetate), is reported here.

Anderegg et al. have reported[3] that either hydrazine or $NaBH_4$ reduction of the dimers $[(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)]$ and $K_2[(NTA)Tc(\mu\text{-}O)_2Tc(NTA)]$ gives rise to deep blue, air-sensitive complexes in solution that have a λ_{max} value of 620 nm. We have found that hydrazine reduction of the new Tc(IV/IV) complex $Ba[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]$ (**2**) also yields a deep blue product with an optical spectrum that is very similar to the spectra of the blue solutions described above. However, **2** is not air-sensitive, unlike the previously reported compounds, and has been isolated and fully characterized.

Experimental Section

Ammonium pertechnetate in aqueous solution was obtained as a gift from DuPont/NEN Products, Billerica, MA. ^{99}Tc is a weak β-emitter (0.29 KeV, half life 2.12 × 10^5 yr); therefore, all manipulations were carried out in laboratories approved for the use of low-level radioactivity, by following precautions detailed elsewhere.[4] The ligand 1,4,7-triazacyclononane-N,N',N''-triacetate[5] (TCTA) was prepared by a literature method[5b] and purified by ion-exchange chromatography to remove sodium bromide, following the procedure of Desreux.[6] The complex $Na[TcO(Eg)_2]$ (Eg = ethylene glycolate) was prepared as described by dePamphilis et al.[7] The compound $Na_2[TcO(Eg)(TCTA)]\cdot MeOH$ was prepared via the reaction of $Na[TcO(Eg)_2]$ with 1 equiv of TCTA and 1 equiv of sodium acetate in anhydrous methanol, as described elsewhere.[8] The bis(μ-oxo) Tc(IV) dimers $[(L)Tc(\mu\text{-}O)_2Tc(L)^n$ (L = NTA, H_2EDTA; n = 2-, 0) were prepared by literature methods.[1,2] All other chemicals were of reagent grade and used as received. Cautionary note: Compounds **1c** and **2b** are isolated as double salts of barium perchlorate. Although no problems have been experienced with these complexes to date, perchlorate salts of metal complexes with organic ligands are potentially explosive, and care should be taken when working with these materials.

Absorption spectra were recorded with a Hewlett-Packard 8451A photodiode array spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 283B IR spectrometer from 4000 to 600 cm^{-1} as KBr pellets. Fast atom bombardment mass spectra were measured with a Varian MAT 731 instrument described elsewhere.[9] Voltammetric studies were carried out in differential pulse mode on a PAR Model 174 polarographic analyzer with a rotating-platinum or a dropping-mercury electrode (DME) and a platinum counter electrode. All potentials were referenced to a saturated calomel electrode (SCE), and $[Ru(NH_3)_6]Cl_3$ was used as the internal calibrant. The buffered solutions below were used as the supporting electrolytes; HOAc/NaOAc (pH 3-6); KH_2PO_4/K_2HPO_4 (pH 5-8); Tris-HCl/Tris (pH 7.5-9.5). The ionic strength of buffer solutions was maintained at ~0.1 M. EPR spectra at -100 °C were recorded with a Spex double monochromator equipped with a cooled RCA 31034 photomultiplier tube and photon-counting electronics. Laser excitation at 514.5 nm and 45 mW incident power was obtained with a Coherent Radiation Model 52 tunable ion laser. Slits were set at 250/300/250 μm. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA. Barium and sodium analyses by atomic absorption were performed by Schwarzkopf Laboratories.

Crystallography. X-ray data were collected from a deep blue crystal of $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (**1c**) at room temperature on an Enraf-Nonius CAD4F-11 κ-geometry diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Details of the data collection, reduction, and refinement procedures were similar to those described elsewhere.[10] A total of 9804 reflections ($+h,+k,\pm l$) were collected in the range 3° ≤ 2θ ≤ 50° with the 6383 reflections having $I_o > 2\sigma(I_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (339 variables) using SHELX-76. Final

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R_1 = 0.066, and final R_2 = 0.066. Hydrogen atoms were ignored while Tc, Ba, water oxygen atoms, and atoms of the perchlorate group wre refined anisotropically. The remainder of the structure was refined isotropically. The final difference-Fourier map contained no chemically significant features. After ~7600 reflections had been collected, there was a sudden drop in the intensity standards of ~15%. We do not believe that this was due to instrumental instability and note that similar behavior was observd with the complex $K_2[(NTA)Tc(\mu\text{-}O)_2Tc(NTA)]$.[2] This drop was corrected for at the time of data reduction.

Crystal data are a = 15.128 (1) Å, b = 18.822 (2) Å, c = 15.582 (1) Å, β = 105.43 (7)°, V = 4276.9 Å^3, space group $P2_1/n$, Z = 4, mol wt = 1366.8, ρ(calcd) = 2.122 g cm^{-3}, ρ(measd) = 2.12 g cm^{-3} (suspension, $CHBr_3$/acetone), and μ = 23.9 cm^{-1}. A semiempirical absorption correction was applied.

Preparation of $Na_3[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]\cdot 2MeOH\cdot 2H_2O$ (1a). Method 1. To 174 mg (0.317 mmol) of $Na_2[TcO(Eg)(TCTA)]\cdot MeOH$ in 15 mL of water was added 40 mg of $NaBH_4$. The solution was brought to a gentle boil in a small open beaker with stirring and was allowed to evaporate to near-dryness over 30 min. During this time, the solution turned from turquoise to a deep gold color, and then more slowly to inky blue. The blue solution was diluted to 10 mL with methanol, stripped to dryness by rotary evaporation, redissolved in a minimal volume of methanol, and loaded on a 1.5 × 6 cm silica gel column (E. Merck 6H silica gel, TLC grade). The product was readily eluted from the column with methanol, and it precipitated as a fine solid by the addition of an equal volume of ether. After isolation by suction filtration, the product was washed with acetone and ether and dried on vacuo at room temperature to give 104 mg (65%) of analytically pure complex as the trisodium salt. Anal. Calcd for $C_{26}H_{48}N_6Na_3O_{18}Tc_2$: C, 31.24; H, 4.84; N, 8.41; Na, 6.90. Found: C, 31.20; H, 4.92; N, 8.36; Na, 6.77. IR (Kbr): 3425 (vs), 3200 (sh), 2960 (w), 1600 (vs), 1430 (s), 1390 (vs), 1310 (s), 1280 (m), 1250 (w), 1090 (m), 1070 (m), 1040 (m), 1015 (m), 980 (w), 960 (m), 895 (m), 820 (s), 770 (m), 735 (m), 680 (m) cm^{-1}. Optical spectrum (H_2O; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 656 (sh, 320), 592 (1350), 520 (900), 325 (sh, 6600), 194 (30600)., Negative-ion FABMS (m/z, ion): 832, $[M^{3-} + 2H^+]^-$; 854, $[M^{3-} + H^+ + Na^+]y^-$; 876, $[M^{3-} + 2Na^+]^-$. The series m/z 833, 855, 877 was also prominent in the spectrum. Glycerol adducts of the ionns at m/z 832, 833, 854, 855 (M^- + 92) were found at 924, 925, 946, and 947. $E_{1/2}$(pH 7.35): +0.167 V (reversible; anodic, platinum electrode; −0.77, −1.4 V (cathodic, DME).

Method 2. To 100 mg (0.075 mmol) of $Ba[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]\cdot {}^3/_4Ba(ClO_4)_2\cdot 8H_2O$ (**2b**) in 10 mL of water was added 10 drops of hydrazine hydrate. The deep pink solution turned deep blue immediately. The reaction mixture was loaded onto a short QAE-Sephadex anion-exchange column and eluted with water to remove Ba^{2+} and hydrazine. The product was then eluted from the column with 0.1 M $NaClO_4$ and precipitated with acetone. This product was redissolved in a minimal volume of methanol, the solution was filtered, and the product was reprecipitated from solution with ether. The product was isolated by suction filtration, washed with ether, and dried in vacuo at room temperature to give 70 mg (93%) of $Na_3[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]\cdot 2MeOH\cdot 2H_2O$ that was indistinguishable from the product **1a** prepared as above, as determined by infrrared and UV/visible spectroscopy and by thin-layer chromatography.

Preparation of $Ba_3[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]_2\cdot 8H_2O$ (1b). To 70 mg (0.07 mmol) of $Na_3[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]$ (**1a**) in 5 mL of water was added 5 mL of 0.1 M $Ba(ClO_4)_2$. The solution was filtered, and 30 mL of ethanol was added slowly with stirring to the filtrate. Purple-blue microcrystals of the barium salt were isolated by suction filtration within 1 h, washed well with methanol, and dried in vacuo at room temeperature for 24 h to give 67 mg (92%) of analytically pure product. Anal. Calcd for $C_{24}H_{52}N_6Ba_{1.5}O_{22}Tc_2$: C, 24.41; H, 4.44; N, 7.12. Found: C, 24.50; H, 4.25; N, 6.96.

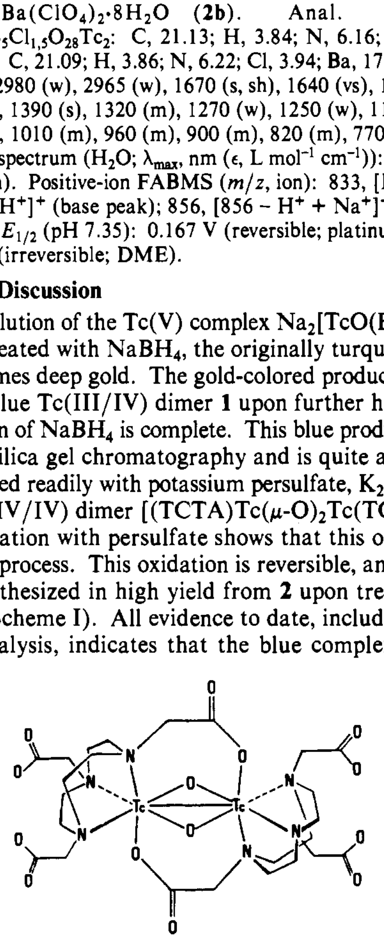
Preparation of $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (1c). The crystals used for the X-ray structure determination were prepared by dissolving the trisodium salt **1a** in water and allowing 0.1 M $Ba(ClO_4)_2$ in ethanol to diffuse into the solution over a period of 1 week at room temperature. A double salt of complex and barium perchlorate was thus isolated. Anal. Calcd for $C_{24}H_{54}N_6Ba_2ClO_{27}Tc_2$: C, 21.09; H, 3.98, N, 6.15; Cl, 2.59; Ba, 20.1; Na, 0.00. Found: C, 21.35; H, 3.90; N, 6.21; Cl, 2.62, Ba, 19.8; Na, 0.00. IR (KBr): 1600, 1580 (vs, ν(COO−)), 1115, 1105, 620 (s, $\nu(ClO_4^-)$) cm^{-1}.

Preparation of $Ba[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]\cdot {}^3/_4Ba(ClO_4)_2\cdot 8H_2O$ (2). To 125 mg (0.125 mmol) of $Na_3[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]\cdot 2H_2O\cdot 2MeOH$ (**1a**) in 10 mL of water was added 17 mg (0.0633 mmol) of potassium persulfate, $K_2S_2O_8$. The deep blue solution became magenta immediately. Addition of 40 mL of acetone precipitated a bright pink solid, which was isolated by suction filtration, washed with acetone, and dried in vacuo. The crude product was separated from K_2SO_4 by flash chromatography on a TLC grade silica gel column (1 × 1.5 cm), which was conditioned and eluted with methanol. The first pink fraction was treated with ether, precipitating a deep pink solid. This was isolated by suction filtration and dried in vacuo to give 100 mg (0.098 mmol, 78%) of product as the disodium salt **2a**.

Alternatively, 3 equiv of $Ba(ClO_4)_2$ in water was added to the above reaction mixture dropwise with stirring. A precipitate of barium sulfate was removed by filtration through fine filter paper. Ethanol (10 mL) was slowly added to the rose filtrate, with stirring. A magenta microcrystalline solid precpitated 30 min. This was isolated by suction filtration, washed well with ethanol, and dried in vacuo at room temperature to give 104 mg (0.076 mmol, 61%) of the double salt $Ba[TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]\cdot {}^3/_4Ba(ClO_4)_2\cdot 8H_2O$ (**2b**). Anal. Calcd. for $C_{24}H_{52}N_6Ba_{1,75}Cl_{1,5}O_{28}Tc_2$: C, 21.13; H, 3.84; N, 6.16; Cl, 3.90; Ba, 17.62. Found: C, 21.09; H, 3.86; N, 6.22; Cl, 3.94; Ba, 17.5. IR (KBr): 3440 (vs, br), 2980 (w), 2965 (w), 1670 (s, sh), 1640 (vs), 1590 (s), 1460 (m), 1430 (m), 1390 (s), 1320 (m), 1270 (w), 1250 (w), 1115 (m), 1105 (m), 1075 (m), 1010 (m), 960 (m), 900 (m), 820 (m), 770 (w), 730 (m) cm^{-1}. Optical spectrum (H_2O; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 350 (sh) 520 (2400) 570 (sh). Positive-ion FABMS (m/z, ion): 833, $[M^{2-} + 3H^+]^+$; 834, $[M^{3-} + 4H^+]^+$ (base peak); 856, $[856 - H^+ + Na^+]^+$; 857, $[834 - H^+ + Na^+)^+$. $E_{1/2}$ (pH 7.35): 0.167 V (reversible; platinum electrode); −0.77 −1.4 V (irreversible; DME).

Results and Discussion

When a solution of the Tc(V) complex $Na_2[TcO(Eg)(TCTA)]$ in water is treated with $NaBH_4$, the originally turquoise solution rapidly becomes deep gold. The gold-colored product is oxidized to the deep blue Tc(III/IV) dimer **1** upon further heating, after decomposition of $NaBH_4$ is complete. This blue product ir readily purified by silica gel chromatography and is quite air-stable. It can be oxidized readily with potassium persulfate, $K_2S_2O_8$, to give the pink Tc(IV/IV) dimer $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ (**2**). Careful oxidation with persulfate shows that this oxidation is a one-electron process. This oxidation is reversible, and compound **1** can be synthesized in high yield from **2** upon treatment with hydrazine (Scheme I). All evidence to date, including a crystal structure analysis, indicates that the blue complex **1** is a Tc(III/IV) mixed-valence dimer of the TCTA ligand, $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{3-}$. This complex represents the first fully characterized Tc–(amino carboxylate) complex in an oxidative state lower than IV. The complex is paramagnetic, as expected for a d^3–d^4 dimer, and solid samples of the complex at −100 °C give a broad EPR signal with a very weak hyperfine splitting pattern of 19 small peaks, as expected for a single electron coupled equally between two Tc atoms with a spin of ${}^9/_2$.



1

Scheme I

$$Na_2[TcO(Eg)(L)] + NaBH_4 \xrightarrow{[R]} \text{gold-colored solution}$$

$$\text{gold-colored solution} \xrightarrow{[O]}$$

$$\underset{\mathbf{1}}{[(L)Tc(\mu\text{-}O)_2Tc(L)]^{3-}} \underset{[R]}{\overset{[O]}{\rightleftharpoons}} \underset{\mathbf{2}}{[(L)Tc(\mu\text{-}O)_2Tc(L)]^{2-}}$$

$$L = TCTA$$

The optical spectrum of this complex in water is dominated in the visible region by an intense band at λ_{max} 592 nm. The visible spectrum of this complex and of the oxidized Tc(IV/IV) complex $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ (**2**) in water are shown in Figure 1. The optical spectrum of the Tc(IV/IV) dimer **2** is quite similar to the spectra of the crystallographically characterized Tc(IV/IV) complexes $[(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)]$[1] and $K_2[(NTA)Tc(\mu\text{-}O)_2Tc(NTA)]$,[2] both of which are dominated by

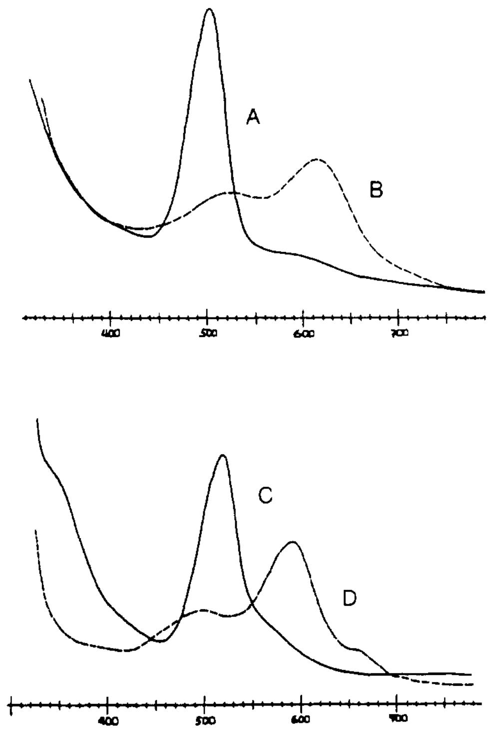


Figure 1. Visible spectra of Tc(IV/IV) and Tc(III/IV) bis(μ-oxo) dimers: (A) [$(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)$]; (B) (A) + hydrazine; (C) [$(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ (**2**); (D) [$(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{3-}$ (**1**) ((C) + hydrazine).

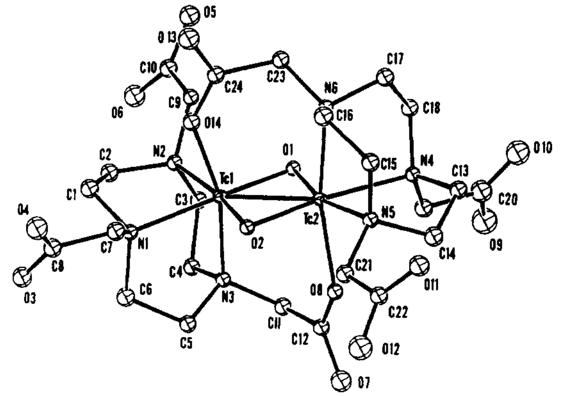


Figure 2. ORTEP diagram of the complex anion of $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (**1c**) showing the atom-numbering scheme and 30% probability thermal ellipsoids.

a strong transition at 500 nm. The spectrum of [$(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)$] is shown in Figure 1 for comparison.

Both the barium and sodium salts of **1** have been prepared. If the material is isolated rapidly from solution, the resulting complex is isolated as either the trisodium salt (**1a**) or with 1.5 barium atoms per dimeric unit (**1b**), indicating clearly that the overall charge on the complex is −3. However, if dilute solutions of $Ba(ClO_4)_2$ in ethanol are allowed to diffuse slowly into an aqueous solution of the trisodium salt, a double salt with barium perchlorate (**1c**) is isolated over 1 week. Both blocks and plates form. The elemental analysis of both crystal types, which can be readily hand sorted, is the same. Preliminary X-ray examination of both types of crystals showed them to have different unit-cell dimensions, but the volumes of the unit cells were the same. The plates invariably decomposed overnight in the X-ray beam, even at low temperature, but the blocks gave a satisfactory data set. The structure determination revealed two bariums per dimeric unit and one perchlorate present for charge balance, as predicted by the elemental analysis.

Table I. Final Positional Parameters for $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (**1c**)[a]

atom	x	y	z
Tc1	0.27378 (6)	−0.31478 (4)	0.46329 (5)
Tc2	0.19343 (6)	−0.20848 (4)	0.48266 (6)
O1	0.3230 (5)	−0.2268 (3)	0.5208 (4)
O2	0.1429 (5)	−0.2965 (3)	0.4240 (4)
O3	0.1832 (6)	−0.5640 (4)	0.3466 (5)
O4	0.1017 (6)	−0.5121 (5)	0.2227 (6)
O5	0.6226 (6)	−0.2626 (4)	0.4579 (5)
O6	0.6121 (6)	−0.3670 (4)	0.5201 (6)
O7	0.1420 (6)	−0.2919 (4)	0.7165 (5)
O8	0.1500 (5)	−0.2453 (4)	0.5911 (5)
O9	0.3611 (7)	−0.0672 (5)	0.7786 (7)
O10	0.3099 (6)	0.0111 (5)	0.6669 (6)
O11	−0.1389 (6)	−0.1233 (4)	0.3892 (5)
O12	−0.1721 (6)	−0.2294 (5)	0.4327 (6)
O13	0.2592 (6)	−0.2503 (4)	0.1991 (6)
O14	0.2734 (5)	−0.2990 (4)	0.3325 (5)
N1	0.2483 (6)	−0.4274 (4)	0.4222 (6)
N2	0.4177 (6)	−0.3519 (4)	0.4933 (6)
N3	0.2857 (6)	−0.3628 (4)	0.5938 (5)
N4	0.2273 (6)	−0.1021 (4)	0.5480 (5)
N5	0.0553 (6)	−0.1595 (4)	0.4409 (6)
N6	0.2135 (6)	−0.1484 (4)	0.3707 (5)
C1	0.3316 (8)	−0.4496 (6)	0.3928 (8)
C2	0.4219 (8)	−0.4260 (6)	0.4581 (7)
C3	0.4511 (7)	−0.3522 (6)	0.5938 (7)
C4	0.3820 (7)	−0.3949 (6)	0.6283 (7)
C5	0.2165 (7)	−0.4208 (6)	0.5745 (7)
C6	0.2332 (8)	−0.4702 (6)	0.4995 (8)
C7	0.1677 (8)	−0.4359 (6)	0.3442 (8)
C8	0.1512 (8)	−0.5110 (6)	0.3037 (8)
C9	0.4741 (7)	−0.2996 (5)	0.4572 (7)
C10	0.5769 (8)	−0.3126 (6)	0.4800 (7)
C11	0.2760 (7)	−0.3170 (6)	0.6721 (7)
C12	0.1829 (7)	−0.2830 (5)	0.6580 (7)
C13	0.1402 (8)	−0.0585 (6)	0.5363 (7)
C14	0.0542 (8)	−0.1053 (6)	0.5143 (8)
C15	0.0452 (8)	−0.1242 (6)	0.3508 (7)
C16	0.1185 (8)	−0.1492 (6)	0.3063 (8)
C17	0.2417 (8)	−0.0722 (6)	0.3983 (7)
C18	0.2880 (7)	−0.0694 (6)	0.4990 (7)
C19	0.2752 (8)	−0.1148 (6)	0.6433 (7)
C20	0.3175 (9)	−0.0492 (7)	0.6992 (9)
C21	−0.0181 (8)	−0.2121 (6)	0.4387 (7)
C22	−0.1164 (8)	−0.1836 (6)	0.4182 (7)
C23	0.2828 (8)	−0.1712 (6)	0.3222 (7)
C24	0.2686 (7)	−0.2450 (6)	0.2800 (7)
Ba1	−0.20667 (4)	−0.32023 (4)	0.54997 (5)
Ba2	0.67016 (4)	−0.14398 (3)	0.38385 (4)
Cl1	0.4904 (3)	0.56577 (18)	0.2324 (2)
O15	0.4359 (8)	0.5631 (6)	0.1433 (7)
O16	0.5799 (9)	0.5604 (12)	0.2298 (10)
O17	0.4699 (7)	0.5095 (5)	0.2836 (6)
O18	0.4727 (16)	0.6290 (6)	0.2692 (10)
OW1	−0.2608 (8)	−0.3864 (6)	0.3814 (6)
OW2	−0.0560 (9)	−0.3868 (7)	0.5081 (10)
OW3	−0.0454 (6)	−0.2550 (5)	0.6610 (7)
OW4	0.4905 (8)	−0.1367 (7)	0.2856 (9)
OW5	0.7505 (10)	−0.1362 (7)	0.5706 (7)
OW6	0.5475 (10)	−0.0720 (8)	0.4602 (10)
OW7	0.0062 (7)	0.3173 (5)	0.7385 (7)
OW8	0.4597 (11)	0.1026 (7)	0.3777 (7)
OW9	−0.0302 (10)	−0.5303 (12)	0.3649 (17)

[a] Numbers in parentheses are errors in the last significant digit(s).

X-ray Structure. The crystal structure of $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (**1c**) reveals a dimeric structure with pseudooctahedral geometry at each technetium. The two technetiums are linked by a planar four-membered $Tc(\mu\text{-}O)_2Tc$ ring. The other four coordination sites on each technetium are filled by a TCTA ligand, bound through an N_3O donor set. One acetate group from each TCTA ligand bridges the two technetium atoms. The remaining acetate groups are coordinated to the barium counterions. The short Tc–Tc distance of 2.402 Å indicates the presence of a metal–metal multiple bond.[11] The four Tc–O bond lengths in the four-membered ring fall between 1.921 (7) and 1.948 (6) Å, with an average distance of 1.936 Å. An ORTEP diagram of the complex is shown in Figure 2. Selected bond distances

Table II. Selected Bond Distances (Å) for $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (**1c**)[a]

Tc1–Tc2	2.4016 (12)	Tc2–O1	1.921 (7)
Tc1–O1	1.936 (6)	Tc2–O2	1.948 (6)
Tc1–O2	1.941 (7)	Tc2–O8	2.088 (8)
Tc1–O14	2.058 (7)	Tc2–N4	2.243 (8)
Tc1–N1	2.218 (8)	Tc2–N5	2.217 (8)
Tc1–N2	2.215 (8)	Tc2–N6	2.167 (9)
Tc1–N3	2.188 (9)	O7–C12	1.242 (15)
O13–C24	1.234 (14)	O8–C12	1.250 (12)
O14–C24	1.295 (13)	N1–C6	1.516 (15)
O3–C8	1.226 (13)	C6–C5	1.565 (17)
O4–C8	1.284 (13)	C5–N3	1.487 (13)
O5–C10	1.268 (15)	N1–C1	1.510 (16)
O6–C10	1.244 (13)	C1–C2	1.508 (14)
C12–C11	1.509 (15)	C2–N2	1.506 (14)
C8–C7	1.540 (16)		

[a] Symmetry operations: (i) $-x, -1 - y, 1 - z$; (ii) $-1 + x, y, z$; (iii) $-{}^1/_2 + x, -{}^1/_2 - y, {}^1/_2 + z$; (iv) $1 - x, -y, 1 - z$; (v) ${}^1/_2 + x, -{}^1/_2 - y, -{}^1/_2 + z$; (vi) $1 + x, y, z$.

Table III. Selected Bond Angles (deg) for the Anion of $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (**1c**)

Tc1–O1–Tc2	77.0 (2)	O2–Tc1–O1	103.2 (3)
Tc1–O2–Tc2	76.3 (2)	O2–Tc2–O1	103.5 (3)
O1–Tc1–O14	103.6 (3)	O1–Tc2–O8	101.8 (3)
O2–Tc1–O14	85.9 (3)	O2–Tc2–O8	85.9 (3)
O14–Tc1–N2	89.9 (3)	O8–Tc2–N5	84.3 (3)
O14–Tc1–N1	84.1 (3)	O8–Tc2–N4	90.7 (3)
N1–Tc1–N2	81.1 (3)	N4–Tc2–N5	81.1 (3)
N2–Tc1–N3	80.8 (3)	N4–Tc2–N6	80.5 (3)
N1–Tc1–N3	80.7 (3)	N5–Tc2–N6	82.5 (3)
N1–Tc1–O2	89.6 (3)	N5–Tc2–O2	89.7 (3)
N3–Tc1–O1	89.8 (3)	N4–Tc2–O1	85.9 (3)
O14–Tc1–N3	163.25 (3)	N6–Tc2–O8	165.1 (3)
O1–Tc1–N1	165.4 (3)	O1–Tc2–N5	165.7 (3)
O2–Tc1–N2	170.2 (3)	O2–Tc2–N4	170.5 (3)
Tc1–N2–C2	110.4 (6)	Tc2–N5–C14	104.7 (5)
N2–C2–C1	113.2 (9)	N5–C14–C13	111.9 (10)
C2–C1–N1	112.7 (9)	C14–C13–N4	111.9 (9)
C1–N1–Tc1	104.7 (6)	C13–N4–Tc2	109.9 (6)
Tc1–N1–C6	109.3 (6)	Tc2–N5–C15	107.9 (7)
N1–C6–C5	111.5 (9)	N5–C15–C16	112.1 (8)
C6–C5–N3	110.0 (9)	C15–C16–N6	111.7 (9)
C5–N3–Tc1	103.7 (6)	C16–N6–Tc2	102.5 (7)
Tc1–N2–C3	105.0 (6)	Tc2–N4–C18	103.6 (6)
N2–C3–C4	107.2 (8)	N4–C18–C17	109.6 (8)
C3–C4–N3	110.2 (8)	C18–C17–N6	109.7 (8)
C4–N3–Tc1	108.8 (7)	C17–N6–Tc2	110.6 (6)
Tc1–N3–C11	120.4 (6)	Tc2–N6–C23	121.3 (6)
N3–C11–C12	114.0 (8)	N6–C23–C24	115.9 (9)
C11–C12–O8	120.7 (10)	C23–C24–O14	117.6 (9)
C12–O8–Tc2	136.2 (7)	C24–O14–Tc1	136.4 (7)

are listed in Table II. Bond angles at technetium and the bond angles of the chelate rings are listed in Table III.

The structure of this Tc(III/IV) dimer shows a strong resemblance in many features to the previously reported structures[1,2] of the Tc(IV/IV) dimers $[(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)]$ and $K_2[(NTA)Tc(\mu\text{-}O)_2Tc(NTA)]$ (Table IV). The planar TcO_2Tc core found in all of these complexes appears to be a relatively rigid entity whose structure is not easily deformed by ligands with different bonding requirements. The Tc–Tc distance in the Tc(III/IV) TCTA dimer is longer than those found in the two Tc(IV/IV) complexes. This may be due to the addition of one electron into an orbital associated with the metal–metal bonding of **1**. If normal bond-ordering arguments hold,[11] this electron should go into an antibonding orbital and thus reduction from Tc(IV/IV) to Tc(III/IV) should lead to an increase in bond length. The lengthened Tc–Tc distance could also be due to the physical constraints of the ligated TCTA. We are attempting to preare crystals of the oxidized dimer $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ (**2**). A crystal structure of this complex will allow a direct comparison of the bond lengths of the reduced and oxidized forms. Such a comparison is important, as theoretical calculations have suggested that normal bond-ordering arguments do not hold in these complexes.[1]

The other four coordination sites on each technetium are filled by the TCTA ligand, through an N_3O donor set. All the ligated Tc–N and Tc–O bonds bend back 5–8° from their expected 90° positions, causing a slight deviation from true octahedral geometry. Two of the nitrogen atoms of each ligand are coordinated in the equatorial plane, trans to the briding oxo groups; the third nitrogen is in an axial position. The four equatorial Tc–N bond distances range from 2.215 (8) to 2.243 (8) Å average 2.22 Å) and are thus slightly longer than the average distances of 2.158, 2.15 (2), and 2.16 Å noted in the structures of $[TcO_2(en)_2]^+$ (en = ethylenediamine), $[TcO_2(tbp)_4]^+$ (tbp = *tert*-butylpyridine), and *trans*-$[Tc(H_2O)(NO)(NH_3)_4]^{2+}$, respectively.[12-14] Presumably, this is due to the trans influence[15] of the briding oxo groups. Long Tc–N bonds (average bond distances of 2.20 Å) were also noted in the crystal structure[1] of $[(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)]$, which also has nitrogen atoms trans to the oxo groups in its TcO_2Tc ring. The two axial Tc–N bonds of **1c** are shorter, at 2.18 Å, but are still slightly longer than are usually[14b] found in other technetium structures. This may be due to the acetate bridge that forms from this position, which is slightly strained.

Two of the acetate groups on each ligand are not bonded to the metal. The third acetate binds axially, cis to the oxo bridge, and bridges the two technetium atoms. The Tc–O(acetate) bond distance of 2.07 Å is slightly longer than the corresponding Tc–O(acetate) bonds in the Tc(IV/IV) bis(μ-oxo) EDTA and NTA dimers (2.02 and 2.03 Å, respectively). This slight lengthening may be due to the fact that the acetate group is part of a bridge from the other technetium atom. Such bridging by a TCTA ligand has not, to our knowledge, been noted previously. The bond angles and bond distances in the triazacyclononane rings are unexceptional;[5b,16] bond angles averaging 109° and N–Tc–N bond angles of 80° are seen in ech of the five-membered chelate rings.

The two barium atoms are eight-coordinate, and their coordination spheres are made up entirely by contacts to oxygen atoms of water molecules and carboxylate groups of the TCTA ligands. The Ba–O distances are unexceptional and range from 2.654 (10) to 2.894 (9) Å.

$[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ (2). When $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{3-}$ (**1**) is treated with strong oxidants, the originally blue complex becomes deep pink, and the product isolated is the Tc(IV/IV) bis(μ-oxo) dimer $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ (**2**). Complex **2** appears to be analogous to the structurally characterized Tc(IV/IV) dimers $(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)$ and $K_2[NTA)Tc(\mu\text{-}O)_2Tc(NTA)]$. These last two dimers can be readily prepared by reduction of TcO_4^- with $NaHSO_3$ in the presence of EDTA or NTA.[1-3] However, these reactions proceed at elevated temperature, and **2** could not be prepared by this method as it is thermally unstable. Attempts at a synthesis of **2** at ambient temperature from pertechnetate, with use of a variety of reducing agents, pH values, and concentrations, failed to give the desired product.

Complex **2** can be isolated as a disodium salt (**2a**) or as a double salt with barium perchlorate (**2b**). The stoichiometry of the barium salt, $Ba[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]\cdot{}^3/_4Ba(ClO_4)_2\cdot$

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Table IV. Comparison of Crystallographically Characterized Tc–(Amino Carboxylate) Dimers

complex	Tc–O, Å	Tc–Tc, Å	Tc–O–Tc, deg	O–Tc–O, deg	ref
$[Tc_2(\mu\text{-}O)_2(TCTA)_2]^{3-}$	1.936 (7)	2.402 (1)	76.6 (3)	103.3 (3)	this work
$[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2]$	1.913 (8)	2.331 (1)	75.4 (2)	104.9 (3)	1
$[Tc_2(\mu\text{-}O)_2(NTA)_2]^{2-}$	1.919 (8)	2.363 (2)	76.0 (3)	104.0 (3)	2

$8H_2O$, is unusual but reproducible. The optical spectrum of $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ (**2**) (Figure 1) is dominated by a band at 520 nm. A transition of this type is characteristic of all the Tc(IV/IV) bis(μ-oxo) amino carboxylate dimers prepared to data and appears to be associated with the presence of the TcO_2Tc core and metal–metal multiple bonding found in all of these complexes. Laser excitation within this band envelope gives rise to Raman spectra where pronounced enhancement of peaks associated with the metal–metal multiple bond and the Tc–O stretch of the TcO_2Tc ring is seen.

Raman Spectrum. A Raman spectrum of $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ in water (0.0002 M) was relatively esy to obtain. Since the Raman experiment is normally an insensitive one, requiring concentrations of ~0.1 M or more for adequate signal to noise,[17] it is apparent that resonance enhancement[11,17,18] is occuring with irradiation at 514.5 nm.

Only four peaks are noted in the spectrum of **2**, at 366, 448, 476, and 748 cm^{-1}. The peak at 366 cm^{-1} lies well within the frequency range expected for a Tc–Tc multiple-bond stretch.[10,1,8] This assignment is only tentative. However, a resonance-enhanced peak at similar frequency has been noted in the resonance Raman spectra of all the Tc(IV/IV) bis(μ-oxo) amino carboxylate dimers studied in this laboratory to date.[19] The corresponding peak in the complex $[(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)]$ is strongly polarized, a fact that is in keeping with its assignment as a M–M stretch.[11,18] The band at 748 cm^{-1}, the strongest band in the spectrum, is tentatively assigned as the Tc–O stretch of the TcO_2Tc ring and falls within the range expected for this peak.[20,21]

The complex $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ underwent apparent photodecomposition during the course of the experiment; the originally pink solution turned deep blue upon prolonged irradiation, and the UV/visible spectrum of this decomposed material matches that of the reduced Tc(III/IV) complex $Na_3[TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]$ quite well. The reaction was photochemical and not thermal, as heating solutions of **2** causes decomposition to a bright yellow, not a blue, product.

The resonance Raman spectrum of $Na_3[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]$ (**1a**) in water (0.0002 M) at 514.5 nm was qualitatively similar to that of **2**, with strong bands seen at 734 and 364 cm^{-1}. These are again tentatively assigned to the Tc–O stretch of the TcO_2Tc core and the Tc–Tc stretch, respectively. Only two other weak bands, at 490 and 448 cm^{-1}, were seen in the spectrum of **1**.

Although it is clear that **2** is a Tc(IV/IV) bis(μ-oxo) dimer, the nature of the donor set bound to technetium in $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$ is unclear at this time. We believe that the potentially hexadentate TCTA ligand in this complex binds as an N_3O donor and that two of the acetate groups are free. If the ligand is bound through an N_3O donor set, the complex should be anionic at pH values above the pK_a of the free carboxylic acid groups and should be cationic at values below this pH. This is, in fact, observed. The complex adheres to anion-exchange resins above pH 6 and to cation-exchange resins below pH 4. The ease with which **1** and **2** are interconverted also suggests that there is no change in the donor set of **1** upon oxidation to **2**. However, conclusive proof of the nature of the donor set in **2** will require a crystal structure determination.

Electrochemistry. As indicated earlier, **1** and **2** are related to one another by a one-electron process and can be chemically interconverted by treatment with hydrazine or persulfate:

$$\underset{\mathbf{2}}{[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}} + e^- \rightleftharpoons \underset{\mathbf{1}}{[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{3-}}$$

The aqueous electrochemistry of the Tc(IV/IV) dimer **2** shows three one-electron-reduction waves. The first of these waves is reversible, and the potential at which it occurs (0.167 V vs SCE) is independent of pH in buffered solutions at pH values between 4 and 8. The electrochemistry of the Tc(III/IV) dimer **1** is identical with that of **2**, except that the first wave is an oxidation wave and not a reduction wave. We believe that the electrode process associated with this first wave is a simple one-electron transfer and that the electrode process corresponds to the chemical transformation noted above.

Evidence for Other Tc(III)/Tc(IV) Amino Carboxylate Dimers. It has been noted[3] that hydrazine reduction of pink solutions of the Tc(IV/IV) bis(μ-oxo) dimers $(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)$ and $K_2[NTA)Tc(\mu\text{-}O)_2Tc(NTA)]$ givs rise to deep blue, air-sensitive complexes in solution. It is our belief that, upon reduction with hydrazine, these bis(μ-oxo) amino carboxylate dimers maintain the TcO_2Tc core in the mixed-valence oxidation state Tc(III/IV). The UV/visible spectra of these blue reduced complexes are very similar to the spectrum of the Tc(III/IV) dimer $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{3-}$ (**1**) (Figure 1). Resonance Raman experiments indicate that the chromophore in the TCTA dimer **1** is associated with the TcO_2Tc moiety. If this chromophore is indeed associated with the $Tc^{III}O_2Tc^{IV}$ structural unit, it seems likely that the TcO_2Tc ring is maintained in all of these complexes, as the chromophore appear in the spectra of all of them.

Unlike the Tc(III/IV) TCTA complex **1**, which is quite air-stable, the deep blue products formed by treatment of the bis(μ-oxo) Tc(IV) dimers of EDTA and NTA with hydrazine are air-sensitive and revert back to their oxidized Tc(IV) starting materials upon aerial oxidation. We have not yet isolated either of these reduced blue complexes. However, we have examined the aqueous electrochemistry of several bis(μ-oxo) Tc(IV/IV) dimers and have found that, as in the electrochemistry of the Tc(IV/IV) dimer $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{2-}$, these dimers undergo three one-electron reductions in water at a dropping-mercury electrode.[19] The first of these reduction waves is reversible, and the $E_{1/2}$ value of this wave is independent of pH at pH values between 6 and 8. We believe that this first electrode process is a simple electron transfer at values above pH 6 and that it corresponds to the formation of a Tc(III/IV) dimer in which the TcO_2Tc core is maintained. The half-wave potential of this reduction wave varies systematically as the donor set in the four sites on each technetium is varied from an N_3O donor set to an NO_3 donor set. The oxidative stability of the chemically reduced deep blue dimers discussed above is such that they are aerially oxidized back to pink Tc(IV/IV) complexes with an ease that is reflected by the potential at which electrochemical reduction takes place.

It appears from these results that the N_3O donor set stabilizes the Tc(III/IV) oxidation state. Whether this is the effect of the triazacyclononane ring or of the bridging acetate groups, a feature that is not seen in the known crystal structures of the Tc(IV/IV) EDTA and NTA complexes, is unclear at this point. The triazacyclononane ring has proved to be a somewhat special ligand, exhibiting a ligand field strength that is not predicted by comparison to that of linear triamines.[22] It has been compared[23] with

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the tripyrazolylborate ligand, which can also stabilize low oxidation states. Our ability to isolate the mixed-valence Tc(III/IV) complex **1** described in this paper demonstrates that the TCTA ligand can be used to stabilize oxidation states that are normally not readily accessible.

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Registry No. **1a**, 115511-93-8; **1b**, 115533-22-7; **1c**, 115511-96-1; **2**, 115511-99-4; Na[TcO(Eg)(TCTA)], 115511-97-2.

Supplementary Material Available: A listing of final thermal parameters for $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (**1c**) (1 page); a listing of structure factors (38 pages). Ordering information is given on any current masthead page.

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Synthesis and Molecular Structure of a "Lantern" Dimer, $(AsPh_4)_2[Tc_2O_2(SCH_2CONHCH_2CH_2NHCOCH_2S)_4]$

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Reaction of $(Bu_4N)[TcOCl_4]$ with a 5-fold excess of *N,N'*-ethylenebis(2-mercaptoacetamide) (H_4ema) in methanolic sodium methoxide yielded a blue precipitate which was metathesized to give $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]$ (**1**). Complex **1** crystallized as a hexahydrate and was structurally characterized by single-crystal X-ray crystallography. The structure of the dianion showed a centrosymmetric dianion with two square-pyramidal $OTcS_4$ cores bridged 4-fold by the $[H_2ema^{2-}]$ dithiolate ligands. The metal–oxo groups are oriented into the center of the cage created by the bridging ligands, giving what is referred to as a "lantern" structure. The intramolecular Tc–Tc* distance was 7.175 (4) Å, and the distance between the two metal oxo ligands, O1–O1*, was 3.96(2) Å. The six water molecules per dimer were found to be hydrogen-bonded to each other and to the amide NH and CO groups on the ligands. Compound **1** was converted to $(AsPh_4)[TcO(ema)]$ when heated in solution or when reacted with aqueous base. Crystal data for **1** are as follows: molecular formula $C_{72}H_{92}N_8O_{16}As_2Tc_2S_8$, monoclinic, $a = 19.099$ (4) Å, $b = 14.144$ (6) Å, $c = 15.809$ (5) Å, $\beta = 109.17$ (2)°, $V = 440033.8$ Å^{-3}, space group $P2_1/n$, $Z = 2$, final $R_1 = 0.067$, $R_2 = 0.103$.

Introduction

Complexes of the d^2 $[OTc^{3+}]$ core are quite prominent in the aqueous chemistry of technetium. Complexes of technetium in the pentavalent oxidation state are characterized by the presence of multiply bonded oxo ligands and a strong affinity for S-containing ligands.[3–6] Stable square-pyramidal complexes of Tc(V) with ethanedithiol,[3] mercaptothioacetate,[4] toluenedithiol,[5] and other dithiolate donors[6] have been prepared. Analogous complexes of technetium(V) with monodentate thiolate ligands are limited to the series of arenethiolate compounds $(AsPh_4)[TcO(SAr)_4]$.[7] Prior to this report no tetrakis(alkanethiolate) complexes $[TcO(SR)_4]^-$ have been characterized.

We have been particularly interested in the coordination complexes of technetium(V) with amide–thiol chelating ligands.[8] Reaction of the tetradentate N_2S_2 ligand *N,N'*-ethylenebis(2-mercaptoacetamide) (H_4ema) with pertechnetate in the presence of a reducing agent produced $[TcO(ema)]^-$ in nearly quantitative yield. The ema ligand spanned the basal plane of the square-pyramidal $[OTc^{3+}]$ core and served as a 4– donor after deprotonation and coordination of the amide and thiolate groups. The complex $(AsPh_4)[TcO(ema)]$ was also prepared by ligand exchange from $(Bu_4N)[TcOCl_4]$ in aqueous methanol. Addition of $(Bu_4N)[TcOCl_4]$ to a 5-fold excess of the ligand H_4ema dissolved in methanolic sodium methoxide gave a transient dark blue color. Heating the reaction mixture or adding aqueous base caused the blue color to fade, giving the yellow complex $[TcO(ema)]^-$ in quantitative yield. We found the transient blue color very intriguing, because the products formed in reactions of dithiol and amide–thiol chelates with technetium(V) are typically bright yellow-orange.[3–6] We repeated the experiment in absolute methanol at room temperature, and the blue compound precipitated from the reaction mixture in good yield. X-ray crystallographic analysis has revealed that this complex has interesting and unusual structural features.

Experimental Section

General Information. *Caution*! ^{99}Tc is a weak β emitter (0.292 MeV, $t_{1/2} = 2.12 \times 10^5$ years); all manipulations of solutions and solids were performed in a monitored laboratory fume hood approved for the handling of radioisotopes, with use of precautions outlined elsewhere.[9] Technetium at $NH_4{}^{99}TcO_4$ in aqueous solution was provided as a gift by Du Pont Biomedical Products. *N,N'*-Ethylenebis(2-mercaptoacetamide)[10] and $(Bu_4N)[TcOCl_4]$[11] were prepared by using standard procedures. All solvents and reagents used were reagent grade and were used as received.

Infrared spectra were measured from 4800 to 400 cm^{-1} on an IBM IR/30S spectrometer with DTGS detector and 2-cm^{-1} bandwidth. ^{1}H

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