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.

Acknowledgment. We gratefully acknowledge the financial support of NEN Products/Du Pont, North Billerica, MA. We thank the Biomedical Research Support-Shared Instrument Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10 RR02243). This investigation was also found (in part) by NIH Grant RR00317, Biotechnology Resources Branch, Division of Research Resources. Part of this work was performed at the MIT Laser Research Center, a National Science Foundation regional instrumentation facility.

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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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

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)°, $V = 440\,033.8$ 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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Table I. Crystallographic Data for $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]$ (**1**)

chem formula	$C_{72}H_{92}N_8O_{16}As_2Tc_2S_8$
fw	1871.84
space group	$P2_1/n$ (No. 14)
a, Å	15.791 (4)
b, Å	14.126 (6)
c, Å	19.069 (5)
β, deg	109.07 (2)
V, Å^3	4020 (4)
d(obsd), d(calcd), g cm^{-3}	1.55, 1.546
Z	2
λ, Å	0.710 69 (Mo Kα)
μ, cm^{-1}	14.59
temp, °C	23
transmission factors	0.66–1.17
R_1	0.067
R_2	0.103

NMR spectra were recorded on a Bruker WM-250 spectrometer. UV–visible absorption spectra were obtained on a Hewlett-Packard 8451A photodiode array spectrophotometer. Fast atom bombardment mass spectra were measured on samples dissolved in triethanolamine (TEA) matrix with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and operating at an accelerating voltage of 8 kV. The FAB gun produced a beam of 6–8 keV xenon neutrals. Raman spectra were recorded on a solid sample sealed in a glass melting point capillary with a Spex 1401 double monochromator equipped with a cooled RCA 31034 photomultiplier tube and photon-counting electronics. Spectra were digitally recorded by using a DEC computer. Laser excitation was at 488 nm with a incident power of 120 nW. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

Preparation of $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]\cdot 3H_2O$ (1). To 260 mg of H_4ema dissolved in 35 mL of 0.11 M sodium methoxide was added a solution of 130 mg of $(Bu_4N)[TcOCl_4]$ (0.26 mmol) in 5 mL of methanol, and the reaction mixture was stirred (12 h). A blue solid precipitate formed, which was filtered, washed with methanol, and redissolved in water. Addition of an aqueous solution of $AsPh_4Cl$ precipitated **1** as a microcrystalline solid. Analytically pure **1** was obtained by recrystallization from 50% aqueous methanol (49%); mp 200 °C dec. Anal. Calcd for $As_2C_{72}H_{80}N_8O_{10}S_8Tc_2\cdot 3H_2O$: C, 46.12; H, 4.58; N, 5.97; S, 13.67. Found: C, 46.00; H, 4.60; N, 5.93; S, 13.38. ^1H NMR (δ; CD_2Cl_2): 1.70 (H_2O), 2.90 (m, 2 H, NCH_2CH_2N), 3.25 (m, 4 H, NCH_2CH_2N and SCH_2CO), 4.90 (m, 2 H, SCH_2CO), 6.97 (br, 2 H, NH), 7.65 (d, 2 H, aryl), 7.79 (tr, 2 H, aryl), 7.90 (tr, 1 H, aryl). IR (cm^{-1}; KBr pellet): 3312 (NH), 1659 (CO), 962 (TcO). Raman (cm^{-1}; microcrystalline solid): 965. UV–vis (λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}); in MeOH): 230 (29 300; $AsPh_4^+$), 258 (25 400), 372 (4630), 610 (1660). Negative mode FABMS (m/z; in triethanolamine (TEA)): 1437, 1203, 1186, 1173, 1157, 1056, 1039, 848, 832, 816, 640, 385, 319 (peak assignments can be found in Table III).

Reaction of 1 with Aqueous Base. To a methanol solution of **1** was added an equal volume of 1 M NaOH, and the solution immediately turned bright yellow. Slow evaporation of the solvent yielded $(AsPh_4)[TcO(ema)]$, which was indistinguishable from authentic material.[8]

X-ray Crystal Structure of $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]\cdot 6H_2O$ (1). Recrystallization from cold 50% aqueous methanol gave **1** as deep blue hexagonal crystals. A blue hexagonal crystal having the approximate dimensions 0.250 × 0.250 × 0.300 mm was mounted on a glass fiber directly from the mother liquor and immediately sealed in epoxy to protect against desolvation. Measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator (see Table I). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using 25 reflections in the range $34.41 < 2\theta < 35.04°$. Weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans), and the counts were accumulated to assure good counting statistics. Solution and refinement were carried out by using the TEXAN programs of the Molecular Structure Corp. The structure was solved by using Patterson methods, and an empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. Due to the limited number of data, carbon, nitrogen, and oxygen atoms on the anion were refined isotropically. The immediate coordination sphere and cation were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d(C–H) = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the B_{equiv} value of the atom to which they were bonded. Crystal data are given in Table I, and final parameters are given in Table II. A complete report of the crystallographic study is included in the supplementary material.

Table II. Final Positional Parameters for $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]$ (**1**)

atom	x	y	z
Tc	0.3977 (1)	0.2703 (1)	−0.02123 (8)
As1	0.6892 (1)	0.4649 (1)	0.6308 (1)
S11	0.3546 (3)	0.2690 (3)	0.0864 (2)
S12	0.6057 (4)	0.8174 (4)	0.1260 (3)
S21	0.2449 (3)	0.2903 (4)	−0.0813 (3)
S22	0.5015 (4)	0.5464 (3)	−0.0430 (2)
O1	0.4513 (8)	0.3699 (8)	−0.0196 (6)
O11	0.403 (1)	0.467 (1)	0.1556 (7)
O12	0.431 (2)	0.790 (1)	0.189 (1)
O21	0.174 (1)	0.456 (1)	−0.2096 (7)
O22	0.318 (1)	0.733 (1)	−0.1361 (9)
O97	0.517 (2)	0.618 (2)	0.240 (1)
O98	0.641 (1)	0.819 (2)	0.334 (1)
O99	0.851 (1)	0.472 (1)	0.077 (1)
N11	0.309 (1)	0.526 (1)	0.0490 (8)
N12	0.379 (1)	0.782 (1)	0.067 (1)
N21	0.308 (1)	0.414 (1)	−0.2117 (8)
N22	0.427 (1)	0.644 (1)	−0.1524 (8)
C11	0.282 (1)	0.370 (1)	0.085 (1)
C12	0.337 (1)	0.459 (1)	0.098 (1)
C13	0.359 (1)	0.609 (2)	0.048 (1)
C14	0.321 (2)	0.700 (2)	0.066 (1)
C15	0.437 (2)	0.815 (2)	0.131 (1)
C16	0.505 (1)	0.882 (1)	0.118 (1)
C21	0.216 (1)	0.298 (1)	−0.181 (1)
C22	0.231 (1)	0.398 (1)	−0.202 (1)
C23	0.340 (2)	0.509 (2)	−0.223 (1)
C24	0.387 (1)	0.553 (1)	−0.146 (1)
C25	0.391 (1)	0.725 (1)	−0.1437 (9)
C26	0.449 (1)	0.813 (1)	−0.141 (1)
C27	0.709 (1)	0.516 (1)	0.5420 (8)
C28	0.659 (1)	0.592 (1)	0.511 (1)
C29	0.669 (1)	0.626 (1)	0.450 (1)
C30	0.725 (2)	0.586 (1)	0.412 (1)
C31	0.775 (2)	0.508 (2)	0.450 (1)
C32	0.763 (1)	0.472 (1)	0.513 (1)
C33	0.628 (1)	0.347 (1)	0.606 (1)
C34	0.596 (1)	0.321 (1)	0.5339 (8)
C35	0.547 (1)	0.238 (1)	0.513 (1)
C36	0.534 (2)	0.183 (1)	0.563 (1)
C37	0.568 (2)	0.205 (1)	0.638 (1)
C38	0.616 (1)	0.289 (1)	0.6583 (9)
C39	0.794 (1)	0.456 (1)	0.715 (1)
C40	0.785 (1)	0.449 (1)	0.7856 (9)
C41	0.859 (1)	0.443 (1)	0.849 (1)
C42	0.941 (1)	0.448 (1)	0.840 (1)
C43	0.954 (1)	0.454 (1)	0.772 (1)
C44	0.880 (1)	0.457 (1)	0.708 (1)
C45	0.617 (1)	0.553 (1)	0.6598 (9)
C46	0.527 (1)	0.541 (1)	0.6416 (8)
C47	0.477 (1)	0.610 (2)	0.661 (1)
C48	0.518 (2)	0.693 (2)	0.694 (1)
C49	0.604 (2)	0.706 (1)	0.709 (1)
C50	0.657 (1)	0.636 (1)	0.692 (1)

Results and Discussion

Reaction of $(n\text{-}Bu_4N)[TcOCl_4]$ with 5 molar equiv of H_4ema in methanolic sodium methoxide yielded a blue powder. This was redissolved in water and precipitated by addition of $AsPh_4Cl$ to give blue, microcrystalline $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]\cdot 3H_2O$ (**1**; 49% yield). A dimeric formulation was proposed based on the negative mode fast atom bombardment spectrum (FABMS$^-$) of **1**. The ions observed in the mass spectrum are assigned in Table III.

The presence of a strong absorption at ν_{max} 962 cm^{-1} in the infrared spectrum of **1** is characteristic of a square-pyramidal technetium(V) complex with a multiply bonded oxo group (Tc–O). Absorptions at 1659 and 3312 cm^{-1} were assigned to amide I and II stretches, respectively, and indicated that the amide groups of the ligands were protonated and uncoordinated. There was no band in the region of a SH stretch (2600–2550 cm^{-1}). This suggested thiolate coordination. The ^1H NMR spectrum of **1** showed multiplets corresponding to the ligand backbone at 2.90 (2 H), 3.25 (4 H), and 4.90 ppm (2 H) and a single resonance

Table III. FABMS⁻ of $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]$ (**1**)

m/z	assgn	*m/z*	assgn
1437	$(AsPh_4)[Tc_2O_2(H_2ema)_4]^-$	848	$[Tc_2O_2(H_2ema)_3]^-$
1203	$H(TEA)[Tc_2O_2(H_2ema)_4]^-$	832	$[Tc_2O(H_2ema)_3]^-$
1186	$(1203 - H_3O)^-$	816	$[Tc_2(H_2ema)_3]^-$
1173	$(1203 - CH_2O)^-$	640	$([Tc_2O_2(H_2ema)_2] - H_2)^-$
1157	$(1203 - CH_2O_2)^-$	358	$[TcO(H_2ema)(H_2O)_2]^-$
1056	$([Tc_2O_2(H_2ema)_4]H_2)^-$	319	$[TcO(ema)]^-$
1039	$[Tc_2O(H_2ema)_4]^-$		

Table IV. Selected Distances (Å) and Angles and Torsion Angles (deg) for $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]$ (**1**)

	Distances		
Tc–O1	1.64 (1)	S11–C11	1.83 (2)
Tc–S11	2.365 (5)	C11–C12	1.50 (3)
Tc–S12*	2.337 (5)	C12–O11	1.24 (2)
Tc–S21	2.326 (6)	C12–N11	1.30 (2)
Tc–S22*	2.340 (5)	N11–C13	1.43 (2)
Tc–Tc*	7.175 (4)	C13–C14	1.51 (3)
O1–O1*	3.96 (2)		
	Bond and Torsion Angles		
O1–Tc–S11	106.5 (4)	O1–Tc–Tc*	8.0 (4)
O1–Tc–S12	109.9 (4)	O1–Tc*–Tc	2.3 (1)
O1–Tc–S21*	110.6 (4)	O1–Tc–S11–C211	60.1 (8)
O1–Tc–S22*	109.7 (4)	O1–Tc–S12*–C16*	79.7
S11–Tc–S21	83.2 (2)	O1–Tc–S21–C21	75.5 (8)
S11–Tc–S12*	143.6 (2)	O1–Tc–S22*–C26*	62.8
C–S–Tc (av)	112.0 (6)		

[a] Estimated standard deviations are given in parentheses.

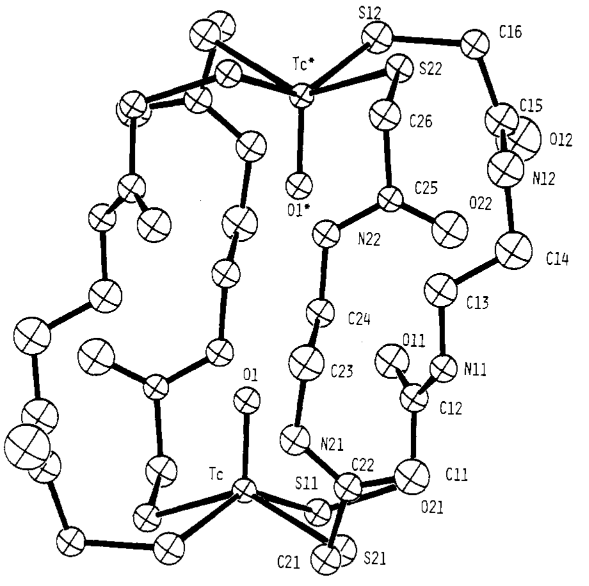

Figure 1. ORTEP drawing of the dianion $[Tc_2O_2(H_2ema)_4]^{2-}$ of **1** showing 30% probability ellipsoids.

for the amide protons at 6.79 ppm (2 H). The aromatic protons for the $AsPh_4^+$ cation were observed between 7.65 and 7.90 ppm (5 H).

The results of the spectroscopic and analytical studies supported the formulation $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]$; however, an unambiguous structural assignment could not be made on the basis of these data. Therefore, the structure was determined by X-ray diffraction. ORTEP drawings of the dianion of **1** are shown in Figures 1 and 2. Selected bond angles and distances are listed in Table IV and as supplementary material.

The dianion of **1** is centrosymmetric and consists of two square-pyramidal $OTcS_4$ cores bridged by four $[H_2ema^{2-}]$ dithiolate ligands. Each technetium atom is positioned 0.769 Å above the S_4 basal plane (mean deviation from the plane 0.0356 Å). The oxo ligand occupies the apical position of each square pyramid. A most interesting feature of this molecule is that the oxo ligands are found inside the cage created by the bridging ligands, giving what shall be referred to as a "lantern" structure.

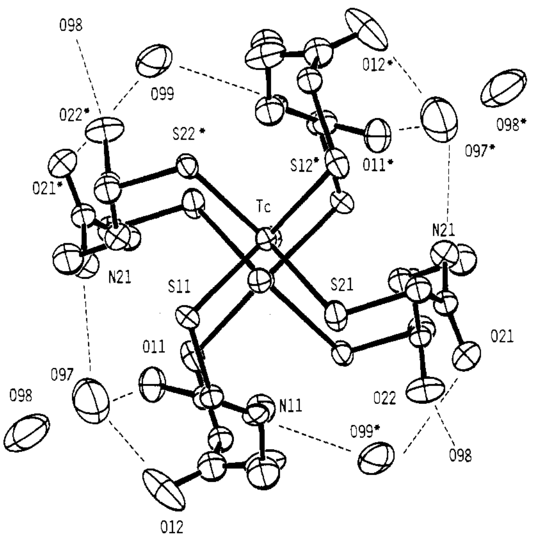

Figure 2. ORTEP drawing (30% probability level) of the dianion $[Tc_2O_2(H_2ema)_4]^{2-}$ of **1** viewed along the Tc–O bonds showing the hydrogen-bonded water molecules about the dianion. Hydrogen-bonding contacts are indicated by dotted lines. Only the relevant oxygen and nitrogen atom labels have been included.

Table V. Hydrogen-Bonding Contacts (Å) for $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]$ (**1**)

O11–O97	2.91 (3)	O97–N21	3.00 (3)
O12–O97	2.80 (3)	O99–N11	2.86 (2)
O21–O99	2.86 (2)	O98–O99	2.73 (3)
O22–O98	2.77 (2)		

[a] Estimated standard deviations are given in parentheses.

The two $OTcS_4$ pyramids in the dimer are oriented such that the Tc–O vectors lie 8° off of a line connecting the two metal centers. The Tc–Tc* and O1–O1* distances are 7.175 (4) and 3.96 (2) Å, respectively.

The Tc–O (1.64 (1) Å) bond distance is in the range observed for other monoxotechnetium(V) complexes (1.610 (4)–1.682 (5) Å)[12] and is directly comparable to other thiolate complexes of technetium(V), $(AsPh_4)[TcO(ema)]$ (1.679 (5) Å),[13] $(Bu_4N)[TcO(SCH_2COS)_2]$ (1.64 (1) Å),[4] and $(Bu_4N)[TcO(SCH_2CH_2S)_2]$ (1.672 (8) Å).[3] The Tc–O stretch observed in the IR spectra of these latter compounds, however, is significantly lower (945 and 933 cm⁻¹) than that observed for **1**. This is possibly due to the orientation of the oxo groups into the center of the lantern. The Tc–S bond lengths for **1** are within the range 2.283–2.485 Å,[14] which is typical of five-coordinate Tc(V) thiolate complexes. The Tc–S–C bond angles averaged 109.2°. Bond lengths and angles for the organic portions of the molecule and the $AsPh_4^+$ cations are unexceptional.

Three water molecules were located per asymmetric unit (six per dimer). These are hydrogen-bonded to each other and to the amide NH and CO groups on the ligands. An ORTEP drawing of a view down the Tc–O bonds shows the hydrogen bonding of the water molecules around the dianion of **1**. The hydrogen-bonding contacts are listed Xn Table V. None of the water molecules were within bonding distance of the metal center.

The electronic spectrum of **1** is quite different from those for $(AsPh_4)[TcO(ema)]$ and other complexes of technetium(V) with

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(14) The dipole moment was calculated by using the Tc–O bond length (1.64 Å), the Pauling electronegativities for Tc and O and the equations found in: Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; pp 160–163. The estimate given here is reasonable in comparison with other X═O double-bonded species (X = C, P, S, Se, and Te), which have dipole moments in the range of (7.0–10.0) × 10^{-30} C m.

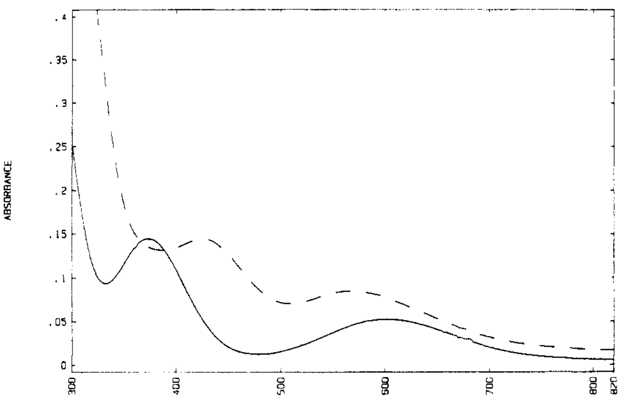
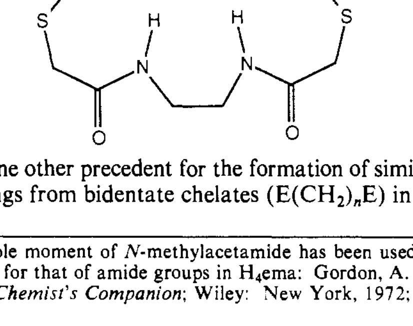


Figure 3. Electronic spectra of $(AsPh_4)_2[Tc_2O_2(H_2ema)_4]$ (**1**, solid line) and $(Bu_4N)[TcO(SPh)_4]$(dashed line) in methanol.

chelating dithiolate ligands, which do not show an absorption maximum above 500 nm.[3-6] The thiolate ligands in **1** are monodentate, and thus, its electronic spectrum more closely resembles the spectra of the monodentate tetrakis(arenethiolate) complexes $[TcO(SAr)_4]^-$ (Ar = Ph, 2,3,5,6-(Me)$_4$Ph, and 2,4,6-(Pr^i)$_3$Ph).[9] The UV–visible spectra of these complexes are nearly identical and show three distinct bands at ca. 260 nm (ϵ = 52 000 L mol^{-1} cm^{-1}), 425 nm (5500), and 575 nm (3300). The spectra of **1** (solid line) and $(Bu_4N)[TcO(SPh)_4]$ (dashed line) are shown in Figure 3 for comparison. The bands at 425 and 575 nm are responsible for the dark red color of $[TcO(SAr)_4]^-$. For compound **1**, only the lowest energy transition (610 nm) occurs in the visible region, and as a result, compound **1** is blue.

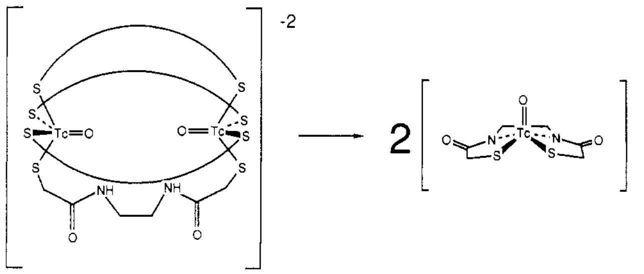
The UV–visible and IR spectra of the precipitate isolated directly from the reaction mixture (prior to precipitation with $AsPh_4Cl$) showed bands directly assignable to the dianion of **1**. The UV–visible spectrum showed an absorption at 610 nm in water, and the IR spectrum showed stretches at 962 (TcO), 1658 (CO), and 3312 (NH) cm^{-1}. The positive mode mass spectrum (FABMS$^+$) showed only Na$^+$ ion peaks. This substance was formulated as the corresponding sodium salt of the lantern, i.e. $Na_2[Tc_2O_2(H_2ema)_4]$.

Complex **1** can be viewed as an inorganic tricyclo compound made of 22-membered $(TcSCCNCCNCCS)_2$ rings. The formation of rings this size in good yields is rather remarkable. Dipole–dipole interactions between the amide groups on the ligands and the metal–oxo group might play a role in organizing the ligands and favor the inclusion of the oxo ligand inside the lantern and away from the solvent. The dipole moment of the Tc–O group is estimated[14] to be 9.0×10^{-30} C m. Since amide compounds (12.7×10^{-30} C m)[15] are considerably more polar than methanol (5.67×10^{-30} C m),[15] the strongest dipolar interactions would occur between the Tc–O group and the amide groups on the ligands. Coordination of the thiolate portion of the ligand and interaction of the oxo (δ^-) and the amide NH groups (δ^+) suggests an orientation that would favor cyclization and the formation of **1**. The presence of four bridging ligands in **1** is attributed to the preference of the oxotechnetium(V) core for thiolate ligands and the stability of the $OTcS_4$ core.[3-6]



There is one other precedent for the formation of similarly large inorganic rings from bidentate chelates ($E(CH_2)_nE$) in which the donor atoms (E) are well separated ($n > 6$). The dimeric bis(diphosphine) complexes *trans*-$[PdCl_2(Bu^t_2P(CH_2)_8PBu^t_2)]_2$ and *trans*-$[RhCl(CO)(Bu^t_2P(CH_2)_8PBu^t_2)]_2$ were recently isolated by Shaw and co-workers.[16] The explanation[17] for the formation of the dimers in their case is based primarily on steric interactions and is, in essence, an extension of the well-known Thorpe–Ingold "*gem*-dimethyl effect".[18]

Complex **1** and the corresponding sodium salt $Na_2[Tc_2O_2(ema)_4]$ decomposed immediately and quantitatively in aqueous basic solution to give 2 equiv of the yellow monomeric complex $(AsPh_4)[TcO(ema)]$. The conversion also occurred slowly in organic solution and more rapidly when the solution was heated. This indicates that while the lantern **1** forms readily in the presence of an excess of the ligand under mild conditions, the thermodynamically favored product is the anionic monomer $[TcO(ema)]^-$. This is expected from consideration of the chelate effect, which would favor coordination of the amide groups.



The isolation of **1** and clean conversion of **1** to $[TcO(ema)]^-$ might have some consequences on the design and coordination chemistry of thiol-containing ligands with technetium. In reactions where there is an excess of a chelating thiolate ligand, formation of tetrakis(thiolate) complexes is possible. If a chelating ligand $HS(CH_2)_xE$, for instance, contains an extremely poor donor atom (E) relative to a monodentate thiolate ligand, or if chelation would result in the formation of large chelate rings ($x > 3$), rearrangement of tetrakis(thiolate) intermediates might become a contributing factor in the formation of the chelate complex.

The isolation of the lantern species in this report is most likely a consequence of the reaction conditions. Certainly, one would not expect to form dimers under the conditions commonly employed for radiopharmaceutical preparations, where the low concentration of the metal, [Tc] $\approx 10^{-8}$ M,[19] would preclude a reaction involving two metal centers. However, the ligand is typically in large excess relative to the metal in these reactions ([ligand] $\approx 10^{-3}$ M) and the possibility of initially forming tetrakis(thiolate) complexes exists.

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Registry No. **1**, 115857-68-6; **1**$\cdot 6H_2O$, 115938-40-4; $(AsPh_4)[TcO(ema)]$, 115826-87-4; $(Bu_4N)[TcOCl_4]$, 92622-25-8.

Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, temperature factor expressions, bond distances, bond angles, and intermolecular contacts up to 3.60 Å (16 pages); a table of intensity data (22 pages). Ordering information is given on any current masthead page.

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