Both complexes are insoluble in water and nonpolar solvents. Compound **1** is soluble in methanol, ethanol, and acetone and compound **2** in a mixture of dioxane–water only. Decomposition of both is observed in DMF and DMSO.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged. We also thank M. Dartmann for technical assistance. This work has been funded by the German Federal Minister for Research and Technology (BMFT) under Contract No. 05339GAB/3.

Supplementary Material Available: Lists of anisotropic thermal parameters (Table VIII for **1** and Table X for **2**), fractional atomic coordinates for hydrogen atoms (Table IX for **1** and Table XI for **2**), and additional interatomic distances and angles (Table XII for **1** and Table XIII for **2**) and the far-IR spectra of **1** and **2** (Figures 7 and 8) (15 pages); lists of observed and calculated structure factors (Table XIV for **1** and Table XV for **2**) (40 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65211

Effect of Ring Size on Properties of Technetium Amine Oxime Complexes. X-ray Structures of $TcO_2Pent(AO)_2$, Which Contains an Unusual Eight-Membered Chelate Ring, and of $TcOEn(AO)_2$

Silvia Jurisson,* Karl Aston,[†] C. Kay Fair,[‡] Elmer O. Schlemper, Paul R. Sharp, and David E. Troutner

Received January 14, 1987

A series of neutral technetium(V) complexes have been synthesized ($TcO(AO)_2$, $TcOEn(AO)_2$, $TcO_2Bn(AO)_2$, and $TcO_2Pent(AO)_2$) in which the length of the hydrocarbon backbone of the amine oxime ligand is varied to effect chemical changes in the resultant complexes. $Pn(AO)_2$, 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime, is the prototype for these ligands. In this series of technetium(V) complexes in which the overall ring size is varied, both monooxo and *trans*-dioxo cores are observed, and an unusual eight-member chelate ring with the technetium(V) center is found with $TcO_2Pent(AO)_2$. $TcO_2Pent(AO)_2{\cdot}CHCl_3$, $TcCl_6O_4N_4C_{17}H_{33}$, crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 1.418$ (2) Å, $b = 13.940$ (7) Å, $c = 18.992$ (10) Å, $\alpha = 69.29$ (4)°, $\beta = 90.00$ (3)°, $\gamma = 83.69$ (3)°, and $Z = 4$. $TcOEn(AO)_2$, $TcO_3N_4C_{12}H_{23}$, crystallizes in the orthorhombic system, space group *Pbca*, with $a = 11.581$ (2) Å, $b = 12.596$ (4) Å, $c = 21.155$ (3) Å, and $Z = 8$.

Introduction

The technetium-99m complex of $Pn(AO)_2$, 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime (Table I), has been shown to be neutral, lipophilic, and able to cross the intact blood brain barrier.[1,2] Recently, we reported the synthesis and characterization of a number of technetium-99-oxo-tetradentate amine oxime complexes in which the substituents on the $Pn(AO)_2$ backbone had been varied.[3] Of these, *dl*-^{99m}TcOHM-PAO has been shown to be an effective cerebral blood flow agent.[4-6]

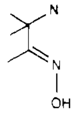
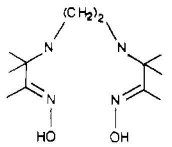
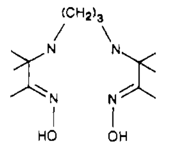
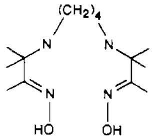
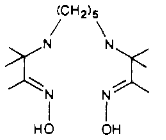
We have been interested for some time in technetium complexes of amine oxime ligands in which the lengths of the hydrocarbon backbones, rather than the substituents on the backbones, are varied to probe the effect(s) on the chemistry of the resultant complexes. The amine oxime ligands of interest are shown in Table I. The amine oxime is varied monotonically from AO, which has no amine–amine hydrocarbon backbone and thus is a bidentate ligand, to $Pent(AO)_2$, which has a five-carbon backbone and forms an unusual eight-member chelate ring on coordination to the Tc(V) center. This series allows the overall macrocyclic ring size about the technetium to be varied from the 13-member $En(AO)_2$ to the 16-member $Pent(AO)_2$ and includes the open-ended member AO.

With these technetium(V) amine oxime complexes we observe both five-coordinate monooxo technetium(V) species (as in $TcOPn(AO)_2$) and six-coordinate *trans*-dioxo technetium(V) species. The syntheses and characterization of $Pent(AO)_2$ and the technetium-99 complexes with these amine oxime ligands are reported.

Experimental Section

General Data. Syntheses were performed with technetium-99, a low-energy (0.292 MeV) β-particle emitter with a half-life of 2.12×10^5 years. When handled in milligram quantities, ^{99}Tc does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination.

Table I. Ligand Nomenclature

ligand	acronym	name
$-CH_2CH_2-$	En	ethylene
$-CH_2CH_2CH_2-$	Pn	propylene
$-CH_2CH_2CH_2CH_2-$	Bn	butylene
$-CH_2CH_2CH_2CH_2CH_2-$	Pent	pentyl
	AO	3-amino-3-methyl-2-butanone oxime or amine oxime
	$En(AO)_2$	3,3,8,8-tetramethyl-4,7-diazadecane-2,9-dione dioxime
	$Pn(AO)_2$	3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime
	$Bn(AO)_2$	3,3,10,10-tetramethyl-4,9-diazadodecane-2,11-dione dioxime
	$Pent(AO)_2$	3,3,11,11-tetramethyl-4,10-diazatridecane-2,12-dione dioxime

---

* To whom correspondence should be addressed. Current address: E. R. Squibb, P.O. Box 191, New Brunswick, NJ 08903.

[†] Current address: 9907 Gilbrook, Rock Hill, MO 63119.

[‡] Current address: Enraf-Nonius, Bohemia, NY 11716.

(1) Troutner, D. E.; Volkert, W. A.; Hoffman, T. J.; Holmes, R. A. *Int. J. Appl. Radiat. Isot.* **1984**, *35*, 467.

0020-1669/87/1326-3576$01.50/0

All common laboratory chemicals were of reagent grade. The AO, En(AO)$_2$, and Bn(AO)$_2$ ligands were available from a previous study and were synthesized and purified as previously described.[7-9] Technetium-99, as a solution of ammonium pertechnetate, was obtained from Oak Ridge National Laboratory, Oak Ridge, TN. Silica gel (NMFC No. 46050) and silica gel 60 TLC plates (catalog no. 5538-7) were obtained from J. T. Baker Chemical Co. and MCB Reagents (Merck), respectively. 1,5-Diaminopentane was obtained from Aldrich Chemical Co. Elemental analyses were performed by MicAnal, Tuscon, AZ.

Pent(AO)$_2$ (3,3,11,11-Tetramethyl-4,10-diazatridecane-2,12-dione Dioxime). Pent(AO)$_2$ was synthesized by a procedure similar to that for Pn(AO)$_2$.[7-9] A 9.214-g (0.068-mol) sample of chloroxime (3-chloro-3-methyl-2-butanone oxime) was dissolved in 40 mL of freshly distilled methanol. The mixture was brought to 0 to -5 °C in an ice–acetone bath, and 3.5 mL (0.030 mol) of 1,5-diaminopentane was added. With stirring the reaction mixture was maintained at 0–5 °C for 2 h, allowed to warm to room temperature, refluxed for 16 h (overnight), and then cooled to room temperature. The solvent was removed by rotoevaporation, and the orange glass was extracted with water and adjusted to pH 10–11 with saturated Na_2CO_3 and NaOH. The gummy white precipitate was filtered and recrystallized from hot methanol. The recrystallized product was filtered out and washed with water, cold methanol, and finally diethyl ether. The product was vacuum-dried. Yield: 5.048 g (56%). Mp: 135–137 °C. Anal. Calcd for $C_{15}H_{32}O_2N_4$: C, 60.00; H, 10.67; N, 18.67. Found: C, 59.15; H, 10.72; N, 18.67. ^{1}H NMR (dmso-d_6): 1.112 (singlet, 12 H, $-CH_3$), 1.281 (multiplet, 6 H, $-CH_2-$), 1.697 (singlet, 6 H, $-CH_3$), 2.177 (multiplet, 4 H, $-CH_2-$), 10.402 ppm (singlet, 2 H, N–OH). ^{13}C NMR (dmso-d_6): 8.978 ($-CH_3$), 24.861 ($-CH_2-$), 25.747 ($-CH_3$), 30.364 ($-CH_2-$), 42.726 ($-CH_2-$), 56.746 (quaternary C), 160.202 ppm (C=N).

Synthesis of TcO(AO)$_2$. To 0.018 g (0.16 mmol) of AO dissolved in 2 mL of H_2O were added 1.60 mL of 0.0309 M NH_4TcO_4 (0.049 mmol) and 2–3 mL of 1 M $NaHCO_3$ (to pH 8–9). While the mixture was stirred, 0.017 g (0.064 mmol) of $SnC_4H_4O_6$ in 1–2 mL of H_2O was added dropwise. The reaction mixture was stirred at room temperature for 10 min and filtered, and the filtrate was then rotoevaporated to $\sim ^1/_2$ mL. The orange-yellow product was extracted into $CHCl_3$; the resultant mixture was dried through anhydrous Na_2SO_4 by gravity filtration and then rotoevaporated to dryness. The residue was taken up in a minimum volume of $CHCl_3$ ($\sim ^1/_2$ mL), diethyl ether was added, and the solution was placed in the freezer to crystallize. The orange crystalline product was filtered out, washed with ether, and air-dried. Yield: ~35–40%. Anal. Calcd for $TcO_3N_4C_{10}H_{21}$: C, 34.88; H, 6.10; N, 16.28. Found: C, 33.60; H, 5.58; N, 15.27.

Synthesis of TcOEn(AO)$_2$. A 0.054-g (0.209-mmol) sample of En-(AO)$_2$ was dissolved in 10 mL of H_2O and 1 drop of 5 M HCl. A 3.10-mL portion of 0.0364 M NH_4TcO_4 (0.113 mmol), 2 mL of 1 M $NaHCO_3$ (to pH 8–9), and 30 mL of diethyl ether were added. While the mixture was stirred, 0.079 g (0.296 mmol) of $SnC_4H_4O_6$ in 2 mL of H_2O was added dropwise. The reaction mixture was stirred at room temperature for 10 min. The yellow ether layer was collected, and the aqueous layer was exhaustively extracted with ether. The combined ether fractions were dried through anhydrous Na_2SO_4 by gravity filtration and then rotoevaporated to dryness. The residue was taken up in a minimum volume of ether, and the resultant mixture was allowed to crystallize in the freezer. The orange crystalline product was filtered out, washed quickly with cold ether, and air-dried. Yield: ~40–50%.

Synthesis of TcO$_2$Bn(AO)$_2$. A 0.020-g (0.070-mmol) sample of Bn-(AO)$_2$ was dissolved in 5 mL of H_2O and 2 drops of 5 M HCl. A 1.50-mL portion of 0.0338 M NH_4TcO_4 (0.051 mmol) and 2–3 mL of 1 M $NaHCO_3$ (to pH 8–9) were added. While the mixture was stirred, 0.017 g (0.064 mmol) of $SnC_4H_4O_6$ in 1–2 mL of H_2O was added dropwise, followed by 20–30 mL of $CHCl_3$. The reaction mixture was stirred at room temperature for 10 min. The greenish gold $CHCl_3$ layer was collected, and the aqueous phase was exhaustively extracted with $CHCl_3$. The combined $CHCl_3$ fractions were dried through anhydrous Na_2SO_4 by gravity filtration and rotoevaporated to dryness. The residue was taken up in a minimum volume of methanol. the product was purified on a silica gel column prepared in methanol. The desired TcO$_2$Bn(AO)$_2$ was eluted as a green-gold band. The purified TcO$_2$Bn-(AO)$_2$ was rotoevaporated to dryness, and the residue was taken up in a minimum volume of diethyl ether. The resultant mixture was filtered and placed in the freezer to allow crystallization. The golden precipitate was collected, washed with pentane, and air-dried. Yield: ~40–45%.

Table II. Crystal Data, Data Collection Parameters, and Refinement Parameters

	TcOEn(AO)$_2$	TcO$_2$Pent(AO)$_2$·2CHCl$_3$
formula	$TcO_3N_4C_{12}H_{23}$	$TcO_4Cl_6N_4C_{17}H_{35}$
fw	369.34	670.21
space group	*Pbca*	$P\bar{1}$
a, Å	11.581 (2)	11.418 (2)
b, Å	12.596 (4)	13.940 (7)
c, Å	21.155 (3)	18.992 (10)
α, deg	90	69.29 (4)
β, deg	90	90.00 (3)
γ, deg	90	83.69 (3)
V, Å^3	3086.0 (5)	2808.0 (8)
Z	8	4
D_{calcd}, g/cm^3	1.590 (1)	1.585 (2)
cryst size, mm	0.25 × 0.3 × 0.4	0.3 × 0.2 × 0.2
μ, cm^{-1}	9.22	11.06
rel transmission factors	92.6–99.7	94.0–99.9
scan method	$\theta-2\theta$	$\theta-2\theta$
scan range, deg θ	$0.56 + 0.35 \tan \theta$	$0.45 + 0.35 \tan \theta$
scan speed	to give 3% counting statistics up to a max of 90 s	to give 4% counting statistics up to a max of 90 s
no. of reflcns measd	4018	7118
no. of indep reflcns	2034	6855
no. of indep reflcns above 2σ used in refinement	1732	5121
no. of variables	274	653
hkl range collcd	h,k,l (2θ = 4–45°) $h,\bar{k},l$ (2θ = 4–40°)	$\pm h,\pm k,l$
θ range, deg	45 in 2θ	44 in 2θ
$R(F)$	0.022	0.043
$R_w(F)$	0.034	0.059
max shift error on last cycle	0.10	0.40

Synthesis of TcO$_2$Pent(AO)$_2$. A 0.030-g (0.10-mmol) sample of Pent(AO)$_2$ was dissolved in 5 mL of H_2O and 1 drop of 5 M HCl. A 1.60-mL portion of 0.0364 M NH_4TcO_4 (0.058 mmol) and 2 mL of 1 M $NaHCO_3$ (to pH 8–9) were added. While the mixture was stirred, 0.017 g (0.064 mmol) of $SnC_4H_4O_6$ in 1–2 mL of H_2O was added dropwise, followed by 30 mL of $CHCl_3$. The reaction mixture was stirred at room temperature for 30 min, and the yellow-orange $CHCl_3$ layer was collected. The aqueous layer was rotoevaporated to ~1 mL and then exhaustively extracted with $CHCl_3$. The various $CHCl_3$ extracts were combined, dried through anhydrous Na_2SO_4 by gravity filtration, and rotoevaporated to $\sim ^1/_2$–1 mL. Diethyl ether was added to the concentrate, and the mixture was placed in the freezer to crystallize. The orange crystalline product was filtered out and washed with ether. The product lost $CHCl_3$ from the crystal lattice on standing. Yield: ~25–30%. A crystal for X-ray diffraction analysis was taken directly from the supernatant and placed in a capillary tube, which was sealed to prevent the loss of $CHCl_3$.

Physical Measurements. Visible–UV spectra were recorded at ambient temperature on an LKB Ultraspec 4050 spectrophotometer interfaced to an Apple IIe computer. The infrared (IR) spectra were recorded as Nujol mulls on a Nicolet 20 DXB Fourier transform infrared spectrometer. The ^{1}H and proton-decoupled ^{13}C NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or dmso-d_6 on a 300-MHz Nicolet NT-300 spectrometer.

Collection and Reduction of X-ray Data. X-ray diffraction data for TcO$_2$Pent(AO)$_2$·2CHCl$_3$ were collected with the crystal mounted and sealed in a capillary filled with $CHCl_3$ vapor because of solvent loss on exposure to the atmosphere. Diffraction data collection, crystal parameters, and refinement information are summarized in Table II. For both

---

(2) Volkert, W. A.; Hoffman, T. J.; Seger, R. M.; Troutner, D. E.; Holmes, R. A. *Eur. J. Nucl. Med.* **1984**, *9*, 511.

(3) Jurisson, S.; Schlemper, E. O.; Troutner, D. E.; Canning, L. R.; Nowotnik, D. P.; Neirinckx, R. D. *Inorg. Chem.* **1986**, *25*, 543.

(4) Holmes, R. A.; Chaplin, S. B.; Royston, K. G.; Hoffman, T. J.; Volkert, W. A.; Nowotnik, D. P.; Canning, L. R. Cumming, S. A.; Harrison, R. C.; Highley, B.; Nechvatel, G.; Pickett, R. D.; Piper, I. M.; Neirinckx, R. D. *Nucl. Med. Commun.* **1985**, *6*, 443.

(5) Chaplin, S. B.; Oberle, P. O.; Hoffman, T. J.; Volkert, W. A.; Holmes, R. A.; Nowotnik, D. P.; Pickett, R. D.; Neirinckx, R. D. *J. Nucl. Med.* **1985**, *26*, p 18.

(6) Sharp, P. F.; Smith, F. W.; Gemmell, H. G.; Lyall, D.; Evans, N. T. S.; Gvozdanovic, D.; Davidson, J.; Tyrell, D. A.; Pickett, R. D.; Neirinckx, R. D. *J. Nucl. Med.* **1986**, *27*, 171.

(7) Murmann, R. K. *J. Am. Chem. Soc.* **1957**, *79*, 521.

(8) Murmann, R. K. *J. Am. Chem. Soc.* **1958**, *80*, 4174.

(9) Vassian, E. G.; Murmann, R. K. *Inorg. Chem.* **1967**, *6*, 2043.

Table III. Visible–UV Spectrophotometric Results[a]

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	shoulders, nm ($\sim\epsilon$, M^{-1} cm^{-1})
$TcO(AO)_2$	278 (6000)	378 (~780) 328 (~2600)
$TcOEn(AO)_2$	283 (5070) 221 (12 000)	390 (~800) 330 (~3000)
$TcOPn(AO)_2$	295 (8080)	360 (~3300)
$TcO_2Bn(AO)_2$	590 (270)	410 (~1500) 289 (~5900)
$TcO_2Pent(AO)_2$		480 (~390) 315 (~2900) 218 (~13 000)

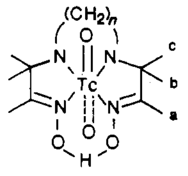
[a] Solvent: methanol. Results for $TcOPn(AO)_2$ from ref 3.

Table IV. Infrared Spectral Results[a]

complex	Tc=O str, cm^{-1}	complex	Tc=O str, cm^{-1}
$TcO(AO)_2$	934	$TcO_2Bn(AO)_2$	784
$TcOEn(AO)_2$	927	$TcO_2Pent(AO)_2$	789, 794
$TcOPn(AO)_2$	923		

[a] IR spectra obtained as Nujol mulls. Results for $TcOPn(AO)_2$ from ref 3.

Table V. ^1H NMR Spectral Results[a]



complex (solvent)	*n*	protons	mult	δ
$TcO(AO)_2$	0	a	singlet	2.254
($CDCl_3$)		b, c	2 singlets	1.376 1.499
$TcOEn(AO)_2$	2	a	singlet	2.165
($CDCl_3$)		b, c	2 singlets	1.351 1.398
$TcOPn(AO)_2$	3	a	singlet	2.226
($CDCl_3$)		b, c	2 singlets	1.365 1.406
$TcO_2Bn(AO)_2$	4	a	singlet	2.286
($CDCl_3$)		b, c	2 singlets	1.406 1.482
$TcO_2Pent(AO)_2$	5	a	singlet	2.160
(CD_2Cl_2)		b, c	2 singlets	1.496 1.540

[a] Only methyl signals are included. Results from ref 3.

compounds the data were collected at 22 (1)°C on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Lattice constants were obtained by least-squares fits of the setting angles of 25 carefully centered reflections for each compound. The intensities of three standard reflections measured after every 7200 s of X-ray exposure showed no significant variation. Orientation was checked after every 200 reflections with the use of three orientation standards. Recentering, using 25 reflections, was done if any of the orientation standards were found to be significantly off center.

Solution and Refinement of the Structures. Both structures were solved by conventional Patterson and Fourier methods. The full-matrix least-squares refinements minimized $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma^2_{counting} + (0.05F_o^2)^2)/4F^2$. Atomic scattering factors were taken from ref 10 and included anomalous scattering contributions. All calculations were done on a PDP 11/34 computer with an Enraf-Nonius SDP package. The maximum electron densities for $TcOEn(AO)_2$ on the final Fourier syntheses were less than 0.5 e/Å^3. The hydrogen atoms were refined in this structure. For $TcO_2Pent(AO)_2$ the residual peaks with intensities of 0.5 to the maximum of 0.95 e/Å^3 were in the vicinities of the disordered $CHCl_3$ molecules. No extinction correction was applied in this structure, and the hydrogen atoms were not refined. The oxime hydrogen position was obtained from a difference Fourier map while all other ligand hydrogens were placed in ideal X-ray positions. Those for the methyl groups were based on the location of at least one peak in a reasonable hydrogen atom position.

Results

The technetium(V) amine oxime complexes were prepared by the reduction of pertechnetate with stannous ion in the presence of ligand. The neutral TcO_xL_y was extracted into either diethyl ether or $CHCl_3$, purified, and isolated.

The visible–UV spectrophotometric data are given in Table III. The infrared spectral data are shown in Table IV. $TcO(AO)_2$ and $TcOEn(AO)_2$ exhibit a Tc=O stretch at ca. 930 cm^{-1}, as expected for a monooxo Tc(V) species. $TcO_2Bn(AO)_2$ and $TcO_2Pent(AO)_2$ do not exhibit a monooxo stretch but rather show absorbances at ca. 790 cm^{-1}, which can be attributed to the asymmetric stretch of the *trans*-dioxo Tc(V) species. The ^1H NMR spectral results are presented in Table V, and the ^{13}C NMR results, in Table VI. The ^1H and ^{13}C NMR spectra are as expected for the amine oxime ligands coordinated to the technetium(V) center.

The X-ray diffraction analysis of $TcOEn(AO)_2$ shows it to be five-coordinate and to have square-pyramidal geometry with the oxo group occupying the apical position, as was found for $TcOPn(AO)_2$.[11] The technetium atom lies 0.768 Å above the plane defined by the four nitrogen atoms. $En(AO)_2$ loses three protons (one oxime and two amine protons) on coordination to form a neutral complex with strong intramolecular hydrogen bonding between oxime oxygen atoms.

The X-ray diffraction study of $TcO_2Pent(AO)_2$ shows it to be six-coordinate and have a slightly distorted octahedral geometry with the technetium atom lying in the plane of the four nitrogens.

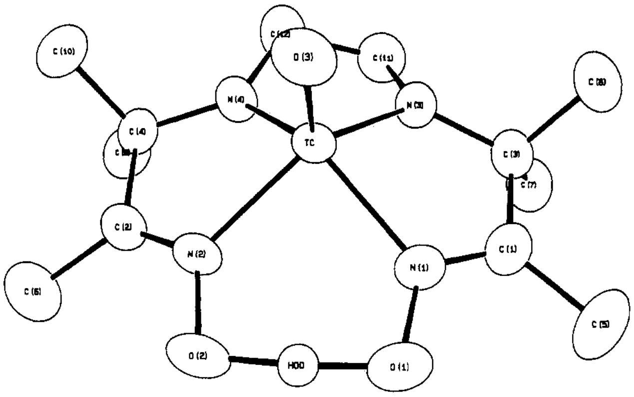


Figure 1. ORTEP representation of oxo(3,3,8,8-tetramethyl-4,7-diazadecane-2,9-dione dioximato(3−)-*N*,*N*′,*N*″,*N*‴)technetium(V), $TcOEn(AO)_2$.

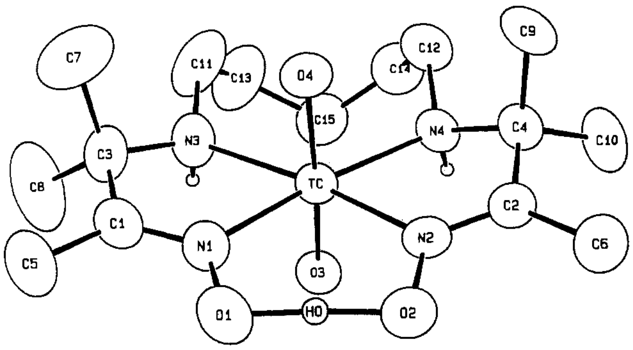


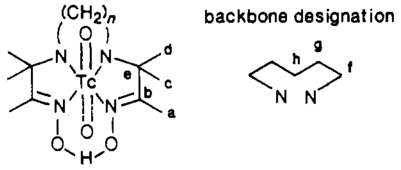
Figure 2. ORTEP representation of *trans*-dioxo(3,3,11,11-tetramethyl-4,10-diazatridecane-2,12-dione dioximato(1−)-*N*,*N*′,*N*″,*N*‴)technetium(V), $TcO_2Pent(AO)_2$.

---

(10) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(11) Fair, C. K.; Troutner, D. E.; Schlemper, E. O.; Murmann, R. K.; Hoppe, M. L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1544.

Table VI. ^{13}C NMR Spectral Results[a]



complex (solvent)	δ						
	n	a, c, d	b	e	f	g	h
$TcO(AO)_2$ $(CDCl_3)$	0	12.338 28.379 28.643	175.021	75.469			
$TcOEn(AO)_2$ $(CDCl_3)$	2	12.450 23.383 25.579	176.259	78.685	59.366		
$TcOPn(AO)_2$ $(CDCl_3)$	3	12.760 23.475 24.011	174.425	79.142	49.650	33.149	
$TcO_2Bn(AO)_2$ $(CDCl_3)$	4	12.975 24.257 24.723	173.306	81.233	51.388	28.388	
$TcO_2Pent(AO)_2$ (CD_2Cl_2)	5	12.410 21.019 24.828	160.032	68.771	45.100	31.293	18.978

[a] Results from ref 3.

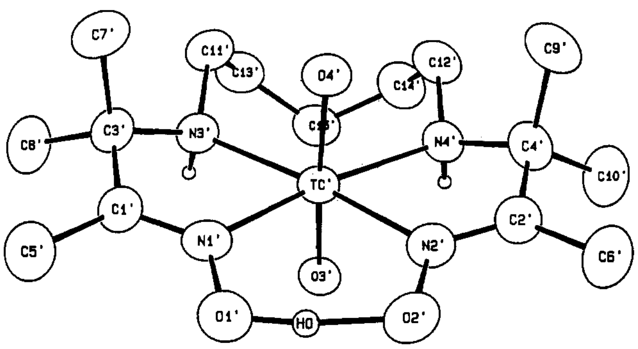


Figure 3. ORTEP representation of *trans*-dioxo(3,3,11,11-tetramethyl-4,10-diazatridecane-2,12-dione dioximato(1−)-N,N',N'',N''')technetium(V), $TcO_2Pent(AO)_2$.

The oxygen–technetium–oxygen bond angle is 170° rather than the ideal 180°. One oxime proton is lost by the $Pent(AO)_2$ ligand on coordination, resulting in a neutral complex with a strong hydrogen bond between oxime oxygen atoms.

Crystal data together with details of the structure determinations are summrized in Table II; atomic fractional coordinates and isotropic thermal parameters are listed in Table VII. Selected bond lengths and bond angles are listed in Table VIII. ORTEP representations are given in Figure 1–4. Parameters for the hydrogen atoms, thermal parameters, listings of observed and calculated structure factors, bond distances and angles not reported, and least-squares planes are available as supplementary material.

Discussion

These technetium(V) amine oxime complexes in which the amine–amine backbone has been varied from a zero- to a five-carbon backbone are unusual. Both the monooxo and the *trans*-dioxo technetium(V) cores are observed for the same class of compounds. Apparently, steric constraints of the amine–amine backbone on coordination are an important factor in this determination (vide infra).

The technetium(V) complexes were prepared by the reduction of pertechnetate in the presence of ligand. The lipophilicity of these neutral complexes is indicated by their partition into diethyl ether and/or chloroform and by their behavior observed on silica gel TLC (methanol solvent): $TcOPn(AO)_2$ (R_f 0.8)[3] > $TcOEn(AO)_2$ (R_f 0.74) > $TcO_2Bn(AO)_2$ (R_f 0.54) ≈ $TcO_2Pent(AO)_2$ (R_f 0.46) > $TcO(AO)_2$ (R_f 0.30). The more lipophilic the complex, the greater is its mobility (R_f value). $TcO_2Bn(AO)_2$ and $TcO_2Pent(AO)_2$, in which the two amine nitrogens are protonated, and $TcO(AO)_2$, in which there is no hydrocarbon backbone, are relatively hdyrophilic when compared with $TcOPn(AO)_2$.

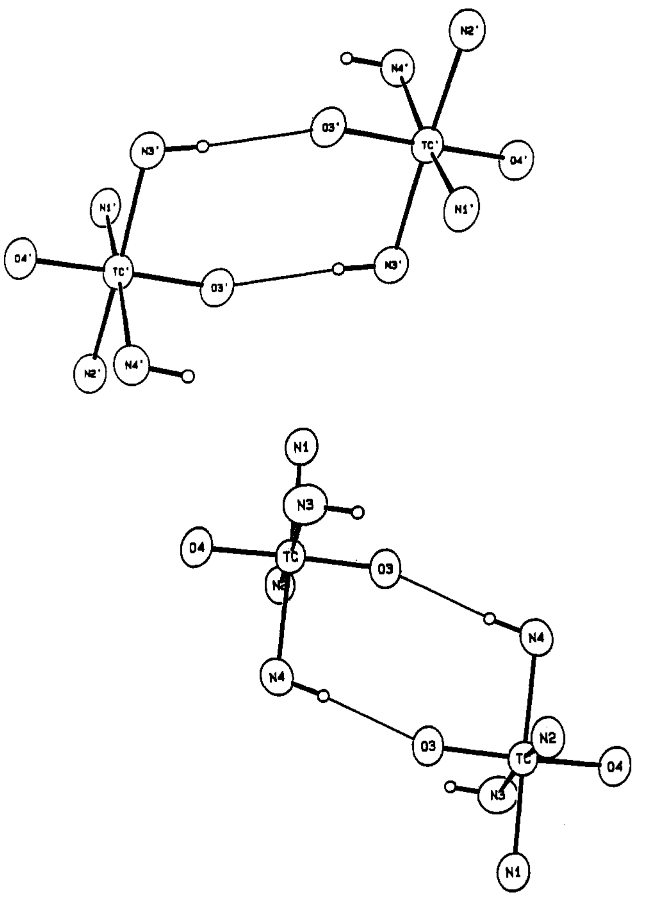


Figure 4. Intermolecular hydrogen bonding between symmetry-related $TcO_2Pent(AO)_2'$ molecules and symmetry-related $TO_2Pent(AO)_2$ molecules. This is not the orientation of the two sets of hydrogen-bonded dimers relative to each other.

The infrared spectra of $TcO(AO)_2$ and $TcOEn(AO)_2$ indicate the presence of the monooxo Tc(V) core with the Tc=O stretch observed at 934 and 927 cm^{-1}, respectively (Table IV). These bands are comparable to those found for $TcOPn(AO)_2$ and its derivatives (908–923 cm^{-1}) (hereafter TcOPnX refers to $TcOPn(AO)_2$ and its derivatives).[3] The IR spectra of $TcO_2Bn(AO)_2$ and $TcO_2Pent(AO)_2$ show no such monooxo vibrations but exhibit fairly intense absorptions in the region characteristic of the *trans*-dioxo Tc=O stretch (750–850 cm^{-1}).[12-14] $TcO_2Bn(AO)_2$ exhibits a band at 784 cm^{-1}, and $TcO_2Pent(AO)_2$, bands at 794 and 789 cm^{-1} (Table IV), which can be assigned as the asymmetric stretch for the O=Tc=O moiety.

The ^1H and ^{13}C NMR spectra (Tables V and VI) do not allow differentiation between the monooxo and the *trans*-dioxo Tc(V) cores. All the spectra are consistent with an amine oxime ligand(s) coordinated to technetium(V). The amine–amine hydrocarbon backbone precludes the equivalency of the four methyl groups adjacent to the amine nitrogens in the *trans*-dioxo complexes.

The X-ray structure of $TcOEn(AO)_2$ shows it to be a five-coordinate, monooxo technetium(V) complex having square-pyramidal geometry (Figure 1). The two amine nitrogens and an oxime oxygen are deprotonated on coordination. The two Tc–N_{amide} bonds are short, as was found for the TcOPnX complexes,

---

(12) Zuckman, S. A.; Freeman, G. M.; Troutner, D. E.; Volkert, W. A.; Holmes, R. A.; VanDerveer, D. G.; Barefield, E. K. *Inorg. Chem.* **1981**, *20*, 2386.

(13) Kastner, M. E.; Lindsay, M. J.; Clarke, M. J. *Inorg.* Chem. **1982**, *21*, 2037.

(14) Kastner, M. E.; Fackler, P. H.; Clarke, M. J. Deutsch, E. *Inorg. Chem.* **1984**, *23*, 4683.

Table VII. Atomic Fractional Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
				TcOEn(AO)$_2$					
Tc	0.14245 (2)	0.15911 (2)	0.12476 (1)	2.353 (6)	C3	−0.0191 (2)	0.2642 (2)	0.0380 (1)	3.36 (6)
O1	−0.0499 (2)	0.0012 (2)	0.1085 (1)	4.65 (5)	C4	0.2065 (2)	0.2321 (2)	0.2506 (1)	2.97 (6)
O2	0.0485 (2)	−0.0103 (1)	0.2117 (1)	4.08 (5)	C5	−0.1614 (3)	0.1068 (3)	0.0111 (2)	5.75 (9)
O3	0.2585 (2)	0.1082 (2)	0.08847 (9)	3.94 (4)	C6	0.1441 (3)	0.0710 (3)	0.3220 (2)	5.08 (9)
N1	−0.0125 (2)	0.1001 (2)	0.0920 (1)	3.12 (5)	C7	−0.1169 (3)	0.3422 (3)	0.0506 (2)	4.44 (8)
N2	0.1080 (2)	0.0831 (2)	0.2090 (1)	2.79 (4)	C8	0.0226 (3)	0.2774 (3)	−0.0299 (2)	5.03 (8)
N3	0.0791 (2)	0.2781 (2)	0.0818 (1)	2.95 (5)	C9	0.1543 (3)	0.3098 (3)	0.2980 (2)	4.25 (8)
N4	0.1813 (2)	0.2628 (2)	0.1851 (1)	3.05 (5)	C10	0.3377 (3)	0.2242 (3)	0.2601 (2)	4.39 (8)
C1	−0.0636 (3)	0.1528 (2)	0.0485 (1)	3.54 (7)	C11	0.1050 (3)	0.3828 (2)	0.1087 (2)	3.73 (6)
C2	0.1507 (2)	0.1237 (2)	0.2586 (1)	2.99 (6)	C12	0.1915 (3)	0.3713 (2)	0.1603 (2)	4.64 (8)
				TcO$_2$Pent(AO)$_2$ and TcO$_2$Pent(AO)$_2$′					
Tc	−0.34312 (4)	0.08952 (4)	0.38872 (3)	2.88 (1)	C12′	0.1332 (6)	0.3050 (5)	−0.0704 (4)	4.0 (2)
O1	−0.1063 (4)	−0.0276 (3)	0.3980 (2)	4.4 (1)	C13′	−0.1394 (6)	0.2315 (5)	−0.0389 (4)	4.0 (2)
O2	−0.2703 (4)	−0.1069 (3)	0.3647 (2)	4.0 (1)	C14′	0.0372 (6)	0.2983 (5)	−0.1238 (4)	4.4 (2)
O3	−0.3601 (4)	0.0200 (3)	0.4838 (2)	3.6 (1)	C15′	−0.0491 (6)	0.2172 (5)	−0.0949 (3)	3.8 (2)
O4	−0.3347 (4)	0.1775 (3)	0.2974 (2)	3.7 (1)	C1S	−0.7128 (8)	0.6578 (6)	0.2876 (4)	6.5 (2)
N1	−0.1616 (4)	0.0610 (4)	0.4032 (3)	3.5 (1)	Cl1	−0.5464 (9)	0.6240 (7)	0.2907 (6)	9.2 (2)*
N2	−0.3647 (4)	−0.0334 (3)	0.3560 (3)	3.2 (1)	Cl2	−0.737 (1)	0.6373 (9)	0.3816 (7)	11.3 (3)*
N3	−0.2919 (5)	0.2147 (4)	0.4262 (3)	4.1 (1)	Cl3	−0.8016 (6)	0.5703 (5)	0.2779 (3)	7.8 (1)*
N4	−0.5356 (4)	0.1009 (4)	0.3688 (3)	3.3 (1)	Cl4	−0.5821 (8)	0.6486 (7)	0.2476 (5)	7.9 (2)*
C1	−0.0978 (6)	0.1260 (5)	0.4133 (3)	4.0 (2)	Cl5	−0.7055 (6)	0.6668 (5)	0.3770 (4)	5.7 (1)*
C2	−0.4630 (6)	−0.0413 (4)	0.3270 (3)	3.4 (1)	Cl6	−0.608 (1)	0.592 (1)	0.2546 (9)	8.7 (4)*
C3	−0.1628 (6)	0.2241 (5)	0.4191 (4)	4.5 (2)	Cl7	−0.6480 (8)	0.6331 (6)	0.3762 (5)	10.1 (2)*
C4	−0.5601 (6)	0.0453 (5)	0.3150 (3)	3.6 (1)	Cl8	−0.8453 (7)	0.5875 (6)	0.3104 (5)	9.5 (2)*
C5	0.0345 (6)	0.1102 (6)	0.4159 (4)	5.5 (2)	Cl9	−0.663 (1)	0.611 (1)	0.2172 (8)	8.2 (3)*
C6	−0.4767 (7)	−0.1284 (5)	0.3000 (4)	5.2 (2)	Cl10	−0.745 (1)	0.577 (1)	0.2470 (9)	8.1 (4)*
C7	−0.1445 (9)	0.3119 (7)	0.3432 (6)	8.5 (3)	C2S	0.2167 (8)	0.3478 (7)	0.6055 (5)	7.2 (3)
C8	−0.1144 (8)	0.2458 (7)	0.4847 (5)	9.2 (3)	Cl11	0.3467 (6)	0.4147 (5)	0.5834 (4)	8.6 (2)*
C9	−0.5601 (7)	0.1167 (6)	0.2325 (3)	4.7 (2)	Cl12	0.2083 (6)	0.3512 (5)	0.6986 (4)	6.3 (2)*
C10	−0.6807 (6)	0.0040 (6)	0.3324 (4)	5.5 (2)	Cl13	0.0667 (8)	0.3636 (7)	0.5777 (5)	11.2 (2)*
C11	−0.3725 (7)	0.3113 (6)	0.4093 (5)	6.9 (2)	Cl14	−0.157 (2)	0.600 (1)	0.495 (1)	11.3 (5)*
C12	−0.6045 (6)	0.2066 (5)	0.3472 (4)	4.6 (2)	Cl15	−0.148 (1)	0.6235 (9)	0.3245 (7)	13.2 (4)*
C13	−0.4713 (8)	0.3091 (6)	0.4571 (5)	6.8 (2)	Cl16	−0.055 (1)	0.616 (1)	0.3786 (8)	8.5 (3)*
C14	−0.6443 (6)	0.2320 (5)	0.4153 (4)	5.0 (2)	Cl17	−0.240 (1)	0.565 (1)	0.4782 (7)	7.8 (3)*
C15	−0.5539 (6)	0.2245 (5)	0.4751 (4)	4.7 (2)	Cl18	−0.254 (1)	0.6240 (9)	0.3101 (7)	12.9 (3)*
Tc′	0.15825 (4)	0.08557 (3)	0.06687 (3)	2.63 (1)	Cl19	0.3030 (6)	0.4304 (5)	0.5489 (3)	7.1 (1)*
O1′	0.2259 (4)	−0.1091 (3)	0.1948 (2)	3.8 (1)	Cl20	0.105 (1)	0.393 (1)	0.5414 (9)	9.3 (4)*
O2′	0.3932 (4)	−0.0356 (3)	0.1205 (2)	3.9 (1)	C3S	0.091 (1)	0.380 (1)	0.1402 (7)	4.2 (3)*
O3′	0.1416 (4)	0.0133 (3)	0.0097 (2)	3.09 (9)	Cl21	−0.0599 (3)	0.4092 (3)	0.1391 (2)	5.6 (1)
O4′	0.1673 (4)	0.1760 (3)	0.1100 (2)	3.43 (9)	Cl22	0.1552 (4)	0.4793 (3)	0.0705 (3)	6.1 (1)
N1′	0.1335 (4)	−0.0345 (3)	0.1643 (2)	3.0 (1)	Cl23	0.1553 (7)	0.3494 (6)	0.2291 (5)	6.0 (2)*
N2′	0.3398 (4)	0.0549 (3)	0.0681 (3)	3.1 (1)	Cl24	0.1499 (7)	0.3858 (6)	0.2270 (4)	5.5 (2)*
N3′	−0.0341 (4)	0.1020 (3)	0.0782 (2)	3.0 (1)	C4S	−0.412 (1)	0.383 (1)	0.1622 (8)	5.0 (3)*
N4′	0.2114 (4)	0.2060 (3)	−0.0375 (3)	3.1 (1)	Cl25	0.6547 (4)	0.4709 (3)	0.1951 (3)	7.1 (1)
C1′	0.0338 (6)	−0.0394 (4)	0.1958 (3)	3.5 (1)	Cl26	0.4405 (4)	0.4146 (4)	0.1491 (3)	7.7 (1)
C2′	0.4047 (5)	0.1185 (4)	0.0254 (3)	3.4 (1)	Cl27	0.6529 (4)	0.3849 (4)	0.0747 (3)	8.0 (1)
C3′	−0.0615 (5)	0.0491 (4)	0.1604 (3)	3.4 (1)	C5S	0.171 (1)	0.375 (1)	0.1430 (8)	5.4 (3)*
C4′	0.3410 (6)	0.2191 (5)	−0.0304 (3)	3.9 (2)	Cl28	0.0896 (4)	0.4622 (3)	0.0652 (2)	7.0 (1)
C5′	0.0164 (7)	−0.1265 (5)	0.2678 (4)	5.0 (2)	Cl29	0.1040 (4)	0.3626 (4)	0.2293 (3)	7.5 (1)
C6′	0.5361 (6)	0.1023 (6)	0.0331 (4)	5.2 (2)	Cl30	0.3098 (4)	0.4210 (4)	0.1455 (3)	7.8 (1)
C7′	−0.0604 (7)	0.1203 (5)	0.2058 (4)	4.5 (2)	C6S	−0.333 (1)	0.373 (1)	0.1598 (9)	5.9 (4)*
C8′	−0.1839 (6)	0.0103 (6)	0.1643 (4)	4.9 (2)	Cl31	0.6029 (9)	0.3969 (7)	0.0720 (5)	7.3 (2)*
C9′	0.3551 (6)	0.3044 (5)	0.0018 (4)	5.1 (2)	Cl32	−0.1869 (4)	0.4103 (3)	0.1394 (3)	7.0 (1)
C10′	0.3944 (7)	0.2421 (6)	−0.1079 (4)	5.5 (2)	Cl33	0.5873 (5)	0.4636 (4)	0.1907 (3)	7.7 (1)
C11′	−0.0995 (6)	0.2082 (5)	0.0427 (4)	3.9 (2)	Cl34	0.6104 (9)	0.3529 (8)	0.0854 (6)	7.8 (2)*

[a] Starred values indicated atoms were refined isotropically.

indicating multiple-bond character (vide infra). The technetium atom is situated 0.78 Å above the plane of the four nitrogens, which is somewhat greater than the average 0.68 (5) Å found for the TcOPnX complexes.[3] The smaller macrocyclic ring size of En(AO)$_2$ adds steric requirements forcing the Tc atom to be situated further above the four-nitrogen plane. The technetium-yl oxygen bond distance of 1.675 (2) Å is in accord with those observed for the TcOPnX complexes.[3] This Tc═O bond distance is at the long end of the range observed for monooxo technetium(V) complexes (1.610 (4)–1.682 (5) Å[3,11,14-18]), indicating the weakening of the Tc═O bond by the multiple-bond character of the two Tc–N$_{\mathrm{amide}}$ bonds (1.89 Å as compared to 2.1 Å for typical Tc—N single bonds[12,13,15]). The amide nitrogens are sp^2 hybridized, as were those in the TcOPnX complexes.[3] The least-squares planes containing the technetium, the amide nitrogen, and the two carbons adjacent to the nitrogen (Tc,N3,C3,C11 and Tc,N4,C4,C12) are close to planar (supplementary material), and the angles about the nitrogen are on the order of 120°, consistent with sp^2-hybridized amide N's. This feature is also observed in the TcOPnX complex.[3]

TcO$_2$Pent(AO)$_2$ is an unusual complex because it exhibits a dioxo core in a series of amine oxime complexes that is largely monooxo and because it forms an eight-membered chelate ring

---

(15) Thomas, R. W.; Estes, G. W.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1979**, *101*, 4581.

(16) Cotton, F. A.; Davison, A.; Day, V. W.; Gage, L. G.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 3024.

(17) Jurisson, S.; Lindoy, L. F.; Dancy, K. P.; McPartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 227.

(18) Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M.; DePamphilis, B.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988.

Table VIII. Comparison of Selected Bond Distances (Å) and Bond Angles (deg)

	$TcOEn(AO)_2$	$TcO_2Pent(AO)_2$	$TcO_2Pent(AO)_2'$	$TcOPn(AO)_2$[a]
Tc–O3	1.675 (2)	1.743 (3)	1.746 (3)	1.679 (3)
Tc–O4		1.744 (3)	1.742 (3)	
Tc–N1	2.062 (2)	2.067 (4)	2.054 (4)	2.093 (4)
Tc–N2	2.063 (2)	2.056 (4)	2.068 (4)	2.086 (3)
Tc–N3	1.900 (2)	2.235 (4)	2.201 (4)	1.908 (3)
Tc–N4	1.881 (2)	2.208 (4)	2.233 (4)	1.917 (3)
N1–O1	1.364 (3)	1.361 (5)	1.365 (5)	1.339 (4)
N2–O2	1.365 (3)	1.370 (5)	1.378 (5)	1.354 (4)
N1–C1	1.279 (4)	1.286 (7)	1.284 (6)	
N2–C2	1.268 (4)	1.284 (6)	1.276 (6)	
N3–C3	1.476 (4)	1.497 (6)	1.522 (6)	1.502 (5)
N4–C4	1.467 (3)	1.527 (6)	1.522 (7)	1.473 (5)
N3–C11	1.468 (4)	1.479 (7)	1.502 (6)	1.463 (5)
N4–C12	1.469 (4)	1.510 (6)	1.488 (6)	1.474 (5)
O3–Tc–O4		170.2 (1)	170.1 (1)	
O3–Tc–N1	133.9 (1)	91.3 (1)	93.5 (1)	108.6 (1)
O3–Tc–N2	111.94 (9)	93.7 (1)	90.9 (1)	110.5 (1)
O3–Tc–N3	113.1 (1)	86.3 (1)	89.6 (1)	110.2 (2)
O3–Tc–N4	112.6 (1)	89.2 (1)	85.5 (1)	110.1 (1)
O4–Tc–N1		92.0 (1)	95.5 (1)	
O4–Tc–N2		95.1 (1)	92.2 (1)	
O4–Tc–N3		85.6 (2)	88.5 (1)	
O4–Tc–N4		88.8 (1)	86.2 (1)	
N1–Tc–N2	87.41 (9)	96.3 (2)	96.6 (2)	85.7 (1)
N1–Tc–N3	77.73 (9)	75.6 (2)	76.5 (1)	77.8 (2)
N1–Tc–N4	133.4 (1)	172.1 (1)	171.9 (1)	141.0 (1)
N2–Tc–N3	134.84 (9)	171.8 (2)	173.1 (1)	139.0 (1)
N2–Tc–N4	77.40 (9)	75.9 (1)	75.4 (1)	77.0 (1)
N3–Tc–N4	82.5 (1)	112.5 (1)	111.4 (1)	92.7 (2)

[a] Results from ref 3.

on coordination. It has a somewhat distorted octahedral geometry (Figures 2 and 3), and $Pent(AO)_2$ loses only an oxime proton on coordination, the two amine nitrogen protons being retained. The average $Tc–N_{amine}$ bond distance of 2.22 Å is in the range observed for Tc–N single bonds (2.0–2.3 Å[12,13,16]), and the average technetium–yl oxygen bond distance of 1.74 Å is typical for *trans*-dioxo technetium(V) complexes.[12,13] There are two independent molecules of $TcO_2Pent(AO)_2$ in the asymmetric unit. The difference between them lies in the hydrogen bonding of an amine proton on one $TcO_2Pent(AO)_2$ to an oxo group of the symmetry-related $TcO_2Pent(AO)_2$. This results in a hydrogen-bonded dimer configuration (Figure 4). $TcO_2Pent(AO)_2$ shows the amine proton on N4 hydrogen bonded to O3 of its symmetry-related molecule, while $TcO_2Pent(AO)_2'$ shows the amine proton on N3′ hydrogen bonded to O3′ on its symmetry-related molecule. The asymmetric unit also contains four $CHCl_3$ molecules. Two $CHCl_3$ molecules are disordered down a channel through the crystal, while the third and fourth $CHCl_3$ molecules are orientationally disordered at two sites.

The complex is somewhat skewed from octahedral geometry presumably due to steric constraints of the $Pent(AO)_2$ ligand. The two trans oxo atoms form a 170° angle with the technetium, and the N3–Tc–N4 angle (the two amine nitrogens and the technetium) is 112°. This particular stability of the anomalous dioxo core for this complex also seems to lie in the steric requirements of the $Pent(AO)_2$ ligand (vide infra).

The distance between N3 and N4 is 3.68 Å in $TcO_2Pent(AO)_2$, while the average N3–N4 distance is 2.72 Å for the TcOPnX complexes and 2.49 Å for $TcOEn(AO)_2$. The pentylene backbone may make conditions very unfavorable for N3 and N4 to be close enough to each other and the technetium to deprotonate, forming two sp^2 amide nitrogens and resulting in the monooxo technetium(V) complex.

Our evidence suggests that the technetium(V) complex with $Bn(AO)_2$ also contains the *trans*-dioxo core, although we cannot eliminate the possibility of $[TcOBn(AO)_2]_2O$ dimer containing a μ-oxo bridge. The similarity of the chemical properties of $TcO_2Bn(AO)_2$ to those of $TcO_2Pent(AO)_2$ suggest a monomer. The UV–visible spectra of $TcO_2Bn(AO)_2$ and $TcO_2Pent(AO)_2$ are significantly different from those of TcOPnX, $TcOEn(AO)_2$, and $TcO(AO)_2$. The IR spectrum shows no monooxo–technetium stretch but does show a band in the region characteristic for the dioxo–technetium stretch. The NMR evidence is not useful in distinguishing the monooxo and *trans*-dioxo cores for the technetium(V) amine oxime complexes. Elemental analysis also allows no discrimination since the calculated values for the monooxo and the *trans*-dioxo complexes are within experimental errors. The chemical properties of $TcO_2Bn(AO)_2$ are much more like those of $TcO_2Pent(AO)_2$ than those of TcOPnX or $TcOEn(AO)_2$. Both $TcO_2Bn(AO)_2$ and $TcO_2Pent(AO)_2$ are significantly more hydrophilic than TcOPnX and $TcOEn(AO)_2$. Their solubilities are also very similar.

Transition-metal complexes with these amine oxime ligands, excluding the $Pent(AO)_2$ ligand, are well established in the literature.[19-22] They coordinate through the amine and oxime nitrogens, and in all cases except those of technetium, the amine nitrogens remain protonated. In this series of technetium(V) complexes we observe cases in which the amine nitrogens are deprotonated and those in which they remain protonated. In a previous study we reported the TcOPnX complexes,[3] in which the amine nitrogens had been deprotonated on coordination and the monooxo technetium(V) core was observed. Here we observe both the monooxo and *trans*-dioxo cores for the same ligand system, the only variant being the amine–amine backbone length and thereby the overall ring size on complex formation. Davison[23] and Deutsch[24] suggest that the electronic nature of the ligands cis to the oxo group is the primary factor in determining whether the TcO^{3+} or *trans*-TcO_2^+ core will be observed. Generally, anionic ligands (e.g., chloride or thiolate), by partially neutralizing some of the charge of the Tc(V) center, induce the formation of the TcO^{3+} core. However, hard, neutral ligands (e.g, amines) and π-acid ligands (e.g., CN^-) favor the *trans*-TcO_2^+ core because of their opposite effect on the electron density at technetium. Both the TcO^{3+} and *trans*-TcO_2^+ cores observed for the technetium(V) amine oxime complexes are consistent with electronic or charge neutralization factors. For the complexes with the TcO^{3+} core, the amine nitrogens of the ligand are negatively charged amide nitrogens and thus help neutralize the charge of the Tc(V) center. Where the *trans*-TcO_2^+ core is observed, the amine nitrogens remain protonated and behave as hard, neutral donor atoms. Therefore, a second oxo group is needed for charge neutralization.

The length of the amine–amine hydrocarbon backbone is the primary difference between the amine oxime ligands forming the TcO^{3+} complexes and those forming the *trans*-TcO_2^+ complexes. This suggests that steric constraints are very important in determining whether the monooxo or *trans*-dioxo Tc(V) core is favored. This is supported by the observation that the technetium(V) complex with AO, which contains no hydrocarbon backbone and thus imposes no steric constraints, contains the monooxo Tc(V) core. Obviously, the monooxo Tc(V) core is favored with these amine oxime complexes. This is in agreement with our argument that more stabilization is obtained through deprotonation and sp^2 hybridization of the amine nitrogens of the ligand and through the formation of two Tc–N multiple bonds as with TcOPnX than is achieved by the formation of the *trans*-dioxo species.[3]

Steric interactions of the pentyl and butyl backbones of $TcO_2Pent(AO)_2$ and $TcO_2Bn(AO)_2$, respectively, constrain the bite angle and coordination bonding distances of the amine nitrogens in such a way to inhibit the formation of the more favorable TcO^{3+} core. In the five-membered ring system with the

---

(19) Schlemper, E. O. *Inorg. Chem.* **1968**, *7*, 1130.

(20) Ching, J. C.; Schlemper, E. O. *Inorg. Chem.* **1975**, *14*, 2470.

(21) Hussain, M. S.; Schlemper, E. O. *Inorg. Chem.* **1979**, *18*, 1116.

(22) Pal, J.; Murmann, R. K.; Schlemper, E. O.; Fair, C. K. *Inorg. Chim. Acta* **1986**, *115*, 153.

(23) Davison, A. In *Technetium in Chemistry and Nuclear Medicine*; Deutsch, E., Nicolini, M., Wagner, H. N., Jr., Eds.; Cortina International: Verona, Italy, 1983, pp 3–14.

(24) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* **1983**, *30*, 75–139.

two-carbon backbone ($TcOEn(AO)_2$) the bite angle of the nitrogens is 82.5 (1)°, the nitrogens are deprotonated and planar, and the N–Tc distances are short. Adding a third carbon to the backbone to make a six-membered ring ($TcOPn(AO)_2$) introduces some change, as shown by the increased bite angle (92.7°). However, the nitrogens are still deprotonated and planar and the Tc–N distances remain nearly the same. The five- and six-membered ring systems are able to accommodate the planar nitrogens without much strain. Increasing the backbone size to five carbons gives an eight-membered ring ($TcO_2Pent(AO)_2$). This increased ring size makes it difficult to maintain a small bite angle and short Tc–N distances without considerable puckering of the ring. This same argument must apply to the seven-membered ring system with a four-carbon backbone ($TcO_2Bn(AO)_2$). In the larger ring systems ring strain inhibits deprotonation of the nitrogens by favoring tetrahedral sp^3 nitrogens and long Tc–N distances.

Acknowledgment. The authors wish to thank Dr. R. B. Taylor for his assistance in obtaining the NMR spectra. Financial support by Amersham International (S.J., K.A., D.E.T.) and the National Science Foundation, Grant No. CH#81-06795 (E.O.S.), is gratefully acknowledged. Support toward purchase of the X-ray instrument by NSF Grant No. CHE 7820347 is also acknowledged.

Registry No. $^{99}TcO(AO)_2$, 109959-88-8; $^{99}TcOEn(AO)_2$, 95180-93-1; $^{99}TcO_2Bn(AO)_2$, 109959-89-9; $^{99}TcO_2Pent(AO)_2$, 109959-90-2; $^{99}TcO_2Pent(AO)_2 \cdot 2CHCl_3$, 109959-91-3; $Pent(AO)_2$, 109929-73-9; chloroxime, 3238-16-2; $NH_4{}^{99}TcO_4$, 34035-97-7; $SnC_4H_4O_6$, 815-85-0; 1,5-diaminopentane, 462-94-2.

Supplementary Material Available: Tables of positional parameters for hydrogen atoms, thermal parameters, bond distances and angles, and least-squares planes (13 pages); listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Physikalische und Theoretische Chemie and Physikalisches Institut, Abt. II,
University of Erlangen-Nürnberg, D-8520 Erlangen, West Germany, and Department of Chemistry,
The Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland

Detailed Study of a Two-Step Quintet ⇌ Singlet Spin Transition in an Iron(II) Complex with a N$_3$O$_2$ Macrocyclic Ligand and the Kinetics of the Quintet → Singlet Relaxation in the Temperature Range 115–130 K

E. König,*[1a] G. Ritter,[1b] J. Dengler,[1b] and S. M. Nelson[2]

Received March 3, 1987

The complicated high-spin (HS, $S = 2$) ⇌ low-spin (LS, $S = 0$) transition in the solid iron(II) complex $[FeL(CN)_2] \cdot H_2O$ of a N_3O_2 macrocyclic Schiff-base ligand L has been studied in detail. When the sample is cooled slowly, a transition from the HS form to a form with approximately equal proportions of HS and LS is observed ($T_c{}^{\downarrow} = 207$ K). The transition is reversible ($T_c{}^{\uparrow} = 222$ K) and, due to the pronounced hysteresis of $\Delta T_c = 15$ K, thermodynamically first order. On reasonably fast cooling (10–20 K min^{-1}) from 300 K to temperatures between 150 and 160 K, the HS form is retained but transforms after several minutes into the LS form. The lower the temperature, the greater the LS fraction. The transformation is irreversible and fast, and below ~150 K it is practically complete. On warming of the LS form, a transformation to the HS:LS = 1:1 form is observed at $T_c = 157$ K. If the sample is rapidly quenched to 77 K, the HS form is frozen in, an irreversible transformation to LS setting in if the sample is warmed to above 110 K. The kinetics of the HS → LS relaxation has been investigated between 115.7 and 130.0 K. The rate constant for the process varies between $k = 6.77 \times 10^{-5}$ and 2.31×10^{-3} s^{-1}, the activation energy being $\Delta E = 7.3$ kcal mol^{-1}. In X-ray diffraction, the transformations are characterized by the replacement of individual diffraction patterns, thus establishing that the unit cells of the forms involved are all different. The quadrupole splitting for the LS form $\Delta E_Q{}^{LS}$ is characterized by a significant dependence on t_{HS}/t_{tot} and thus n_{HS}. It is believed that the dependence arises since the HS form is seven-coordinate, while the LS form is six-coordinate with one ether oxygen of the macrocycle uncoordinated.

Introduction

Recently, we have reported[3] on the synthesis and some unusual properties of the iron(II) complex $[FeL(CN)_2] \cdot H_2O$ with the macrocyclic Schiff-base ligand L derived from the condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine. Magnetic susceptibilities and the ^{57}Fe Mössbauer effect, which were studied over the temperature range 80–300 K, revealed a complex variation of the ground state with temperature. At ambient temperature, the thermodynamically stable form is high spin (HS), evidence being the effective magnetic moment $\mu_{eff} = 5.09\ \mu_B$ and the Mössbauer spectrum characterized by the quadrupole splitting $\Delta E_Q = 3.18$ mm s^{-1} and the isomer shift $\delta^{IS} = +0.84$ mm s^{-1} at 293 K. When the complex was slowly cooled to 225 K, the magnetic moment started to decrease, its value leveling out below ca. 210 K at 3.58 μ_B. Mössbauer-effect measurements showed that the apparently stable form consists of the high-spin (HS) and low-spin (LS) ground states in an almost equal proportion. The transition is reversible, although the transformation to the pure HS state arises at ca. 220 K, i.e. at a somewhat higher temperature. There is therefore a pronounced hysteresis loop associated with the transition. The HS form may be frozen in if the sample is rapidly cooled in liquid nitrogen. Slow warming of the quenched-in HS complex produced an abrupt decrease of the magnetic moment above ca. 110 K from 5.0 to ~1.00 μ_B. On the basis of the Mössbauer study, the result of this transformation is the practically pure LS state of the complex characterized, at 151.2 K, by the values $\Delta E_Q = 1.43$ mm s^{-1} and $\delta^{IS} = +0.28$ mm s^{-1}. If the sample is now slowly warmed up, first a transformation to the HS:LS = 1:1 form is observed around 153 K, followed by the transformation to the pure HS state in the region 200–218 K.

The above results have thus established the existence of a thermally controlled high-spin ($S = 2$) ⇌ low-spin ($S = 0$) transition in the complex $[FeL(CN)_2] \cdot H_2O$. It should be noted that the pure LS state has been obtained separately by way of transformation of the quenched-in HS form at low temperatures. The reversible spin-state transition has thus been established only

---

(1) (a) Institut für Physikalische und Theoretische Chemie, University of Erlangen-Nürnberg. (b) Physikalisches Institut, Abt. II, University of Erlangen-Nürnberg.

(2) Deceased. The Queen's University of Belfast.

(3) Nelson, S. M.; McIlroy, P. D. A.; Stevenson, C. S.; König, E.; Ritter, G.; Waigel, J. *J. Chem. Soc., Dalton Trans.* **1986**, 991.

0020-1669/87/1326-3582$01.50/0