cyclic rings can be inferred from ^{195}Pt–^{1}H coupling data: H(6) of the thymine ligand exhibits sidebands caused by coupling with the ^{195}Pt isotope (J = 37 Hz), as does the NH signal (J = 20 Hz). The relative magnitudes of coupling constants indicate that the site of platinum coordination is closer to H(6) than to the NH group, caused by N(1) being the site of platination. The H(5) signal of 1-methylcytosine is coupled not only to H(6) (J = 8 Hz) but also to ^{195}Pt (J = 20 Hz). This is consistent with N(3)–platinum binding.[22] The H(5) and H(6) signals and the NH_2 signal of 1-methylcytosine are shifted downfield upon platination. The shifts for H(5) and H(6) are relatively minor (approximately 0.1 ppm each); the NH_2 signal shift, however, is substantial (1.50 and 1.75 ppm). It reflects the acidification of the amino protons on platinum coordination at N(3), which is sufficient to allow even substitution of a proton for a second platinum.[23] Splitting of the cytosine amino group signal in a 1:1 ratio indicates nonequivalence of the two protons. It probably is a consequence of the increased hindrance of the NH_2 group to rotation about the C4–N4 bond on platinum binding at N(3).[24] The proton signals of the two NH_3 groups cis to each other are nonequivalent as well and also exhibit ^{195}Pt coupling of approximately 52 Hz each. Only the low-field satellites overlap with the N–CH_3 signal of 1-methylcytosine.

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Registry No. *cis*-$[Pt(NH_3)_2(C_5H_7N_3O)(C_5H_5N_2O_2)]ClO_4$, 73103-92-1.

Supplementary Material Available: A listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Preparation and X-ray Structure of *trans*-Dioxo(1,4,8,11-tetraazacyclotetradecane)technetium(V) Perchlorate Hydrate

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The preparation, properties, and X-ray structure of *trans*-$[Tc(cyclam)O_2]ClO_4{\cdot}H_2O$ are described. The yellow complex crystallizes in space group $P\bar{1}$ with two independent molecules per unit cell, each having a crystallographically imposed center of symmetry: a = 9.964 (3) Å, b = 9.473 (2) Å, c = 11.815 (3) Å, α = 101.38 (2)°, β = 112.54 (2)°, γ = 113.50 (2)°, Z = 2, ρ_{exptl} = 1.72 g cm^{-3}, ρ_{calcd} = 1.728 g cm^{-3}. The structure was solved by using 2671 data having $F > 3\sigma_F$; final R = 0.040, R_w = 0.055. The average Tc–O distance is 1.751 (4) Å, and the average Tc–N distance is 2.125 (11) Å.

Introduction

Technetium-99m is one of the most common radionuclides used for imaging in diagnostic nuclear medicine. For most in vivo uses, the metal, which is available as pertechnetate, must be complexed in a reduced form by ligands which produce complexes that are stable in body fluids and, in the most ideal cases, result in specific biodistributions. At the same time, other criteria must be met such as rapid excretion from the body, etc. As noted by Deutsch,[2] both synthetic Tc chemistry and chemistry of Tc pharmaceuticals are poorly understood. In fact, only recently have inorganic chemists applied their talents to the rational design of technetium complexes of potential pharmaceutical interest.

Recent experiments have shown that robust complexes of ^{99m}Tc, generated from $^{99m}TcO_4^-$ by Sn(II), $Na_2S_2O_4$, or electrochemical reduction, are rapidly formed with macrocyclic tetraaza ligands.[3-5] Because of the relative ease with which the chelate ring sizes, ligand charge and ring substituents can be varied in this class of ligands, these observations suggested that a major advance in the design of complexing agents might be made and investigations in this area are under way. However, one of the difficulties with tracer level experiments is that characterization and subsequent study of the chemistry of the species formed is very difficult because of the extremely low ^{99m}Tc concentrations (i.e., $<10^{-8}$ M) used. In addition, the possibility of forming a ^{99m}Tc complex with impurities in the presumed ligand[6] makes it imperative that the chemistry observed at the tracer level be related to macroscopic technetium chemistry by using long-lived ^{99}Tc. This report concerns the preparation and structure determination of the perchlorate salt of $[^{99}Tc(C_{10}H_{24}N_4)O_2]^+$, the species believed to be formed under similar conditions at the tracer level. This is the first *trans*-dioxotechnetium complex to be structurally characterized, and it has the longest metal–nitrogen bond distances of any cyclam complex whose structure is known. Both of these points are considered further in the Discussion.

Experimental Section

Cyclam was purchased from Strem Chemicals, Inc., and purified by recrystallization from chlorobenzene. Technetium-99 was pur-

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Table I. Crystal Data $[Tc(C_{10}H_{24}N_4)O_2]ClO_4 \cdot H_2O$

mol wt	448.79
dimens, mm	0.45 × 0.30 × 0.13
space group	$P\bar{1}$
cell constants	
a, Å	9.964 (3)
b, Å	9.473 (2)
c, Å	11.815 (3)
α, deg	101.38 (2)
β, deg	112.54 (2)
γ, deg	113.50 (2)
no. of reflcns used to determine cell constants and their 2θ limits, deg	15, $8 < 2\theta < 21$
Z	2
ρ_{calcd}, g cm^{-3}	1.728
ρ_{exptl}, g cm$^{-3\,a}$	1.72

[a] By flotation in hexane-1,2-dibromoethane.

chased from New England Nuclear as $NH_4{}^{99}TcO_4$. All other chemicals were of reagent grade.

Preparation of $[^{99}Tc(C_{10}H_{24}N_4)O_2]ClO_4 \cdot H_2O$. Solid cyclam (0.63 g, 3.1 mmol) was dissolved in 10 mL of 2.77×10^{-2} M $NH_4{}^{99}TcO_4$ (0.28 mmol). To this solution was added 20 mL of 0.062 M $Na_2S_2O_4$ (1.24 mmol) freshly prepared in bicarbonate buffer at pH 11. After 1 h, NaOH pellets were added to the resulting brownish mixture until the NaOH concentration was ~0.1 M. After being cooled, the mixture was extracted three times with $CHCl_3$ to remove excess cyclam. To the aqueous fraction was added 0.06 g of $NaClO_4 \cdot H_2O$ (0.43 mmol). The mixture was filtered to remove a greenish brown solid. A pale orange solution resulted from which yellow-orange crystals formed upon slow evaporation. The solution was allowed to evaporate to dryness, and the crystals were washed several times with a 50:50 v/v ethanol-water mixture followed by a final wash with absolute ethanol. The yield was 8.7 mg (~7%).

Spectral Measurements. Visible–UV spectra of solutions in quartz cells were obtained with the use of a Perkin-Elmer 576ST spectrophotometer. The concentration of $NH_4{}^{99}TcO_4$ in the stock solution was determined by absorption at 245 nm.[7] IR spectra of Nujol mulls on KBr plates were obtained with the use of a Beckman IR-10 spectrophotometer.

Solution and Refinement of the Structure. Crystal data and certain details of the structure refinement are given in Tables I and II, respectively. All computations were performed on a CDC Cyber 74 computer using Sheldrick's SHELX-76 program package with minor local modifications. Scattering factors were taken from the usual source;[8] those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components.[9] The structure was solved by standard heavy-atom methods. After location of all nonhydrogen atoms, these were refined anisotropically for three cycles after which time hydrogen atom positions associated with each atom of the macrocyclic ligand were calculated assuming sp^3 hybridization for the carbon and nitrogen atoms. Hydrogen atoms of the water molecules were not located. In subsequent cycles of least-squares refinement, hydrogen atom positions were held constant and only their isotropic thermal parameters were allowed to vary. In the final cycle of refinement, the thermal parameter of HN2 of molecule 1 was unreasonably large, but it was not considered sufficiently important to delete it and repeat the final cycles of least-squares refinement. Final positional and anisotropic thermal parameters for nonhydrogen atoms are given in Table III. Hydrogen atom positional and thermal parameters and structure factor tables are available as supplementary material.

Results

Synthesis and Characterization of $[Tc(cyclam)O_2]^+$. A cyclam complex of apparent 1+ charge was detected earlier (by electrophoresis) in ^{99m}Tc studies.[5] Its obvious stability to air and both acid and base suggested that it might be isolable. Indeed $[Tc(cyclam)O_2]^+$ is formed in aqueous solution from the reaction of $Na_2S_2O_4$ with TcO_4^- in the presence of excess cyclam. The perchlorate salt crystallizes as yellow orange rectangular plates upon slow evaporation of an aqueous solution. The complex exhibits UV-vis absorptions at 204, 311, and 485 nm in aqueous solution, and the infrared spectrum of the solid contains, in addition to the expected N-H absorptions at 3250 and 3120 cm^{-1}, a band at 3600 cm^{-1}, consistent with the presence of water in the compound, and a moderately intense absorption at 790 cm^{-1} which is absent in Ni(II) and Co(III) complexes of the cyclam ligand. Comparison of the energy of the latter absorption with those of amine complexes of the ReO_2^+ moiety[10] (which fall in the range of 810–820 cm^{-1}) suggested a trans-dioxo structure, a formulation most compatible with the 1+ charge determined in the tracer studies. Electrophoretic and spectral properties of a technetium cyclam complex prepared by use of Sn(II) as a reducing agent were identical with those described above. The dioxo structure is confirmed by the X-ray diffraction results.

Table II. Data Collection and Refinement Details for $[Tc(C_{10}H_{24}N_4)O_2]ClO_4 \cdot H_2O$

diffractometer	Syntex $P2_1$
monochromator (Bragg 2θ angle, deg)	graphite (12.2)
radiation, Å	Mo K$\bar{\alpha}$ (0.710 69)
take off angle, deg	6.75
scan method	$\theta-2\theta$
scan speed, min/max, deg min^{-1}	2.0/29.3
scan width, deg	2.0
bkgd/scan time ratio (TR)^a	1.0
no. of standard reflctns (monitoring frequency, no. of reflctns)	3^b (97)
2θ limits of data, deg	$4 < 2\theta < 50$
h,k,l limits	$-h,-k,0 \rightarrow +h,+k,+l$
no. of data	2976
no. of data used in final refinement $(F > 3\sigma_F)^c$	2671
no. of data/no. of variables	11.9
μ, cm$^{-1\,d}$	26.4
$R = (\Sigma\,\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/(\Sigma\,\lvert F_o\rvert)$	0.040
$R_w = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)(w^{1/2})]/[\Sigma(\lvert F_o\rvert)\cdot(w^{1/2})]^e$	0.055

[a] Background counts measured before (BG1) and at the end (BG2) of the scan. Intensities determined from total scan (CT) and background (BG) counts by $I = CT - TR(BG1 + BG2)$. $\sigma_I = [CT + (TR)^2(BG1 + BG2)]^{1/2}$. [b] Standard reflections were as follows: 6,0,0; 0,5,0; 0,0,8. [c] $F_o = (I/Lp)^{1/2}$; $\sigma_F = \sigma_I/2(F)(Lp)$ where Lp is the Lorentz and polarization correction. [d] Data were corrected for absorption by an empirical method based on ψ scans of reflections near $\chi = 90°$: I_{min}/I_{max} ranged from 0.81 to 0.85. [e] $w = n/(\sigma_F{}^2 + mF^2)$; in the final cycle n was 1.0 and m was 2.9×10^{-3}.

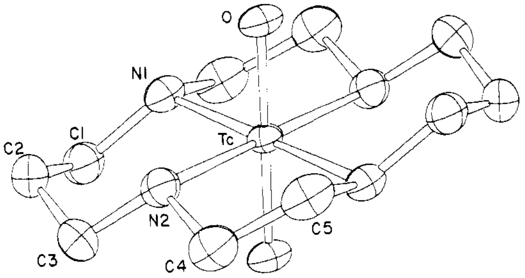

Figure 1. ORTEP drawing of the cation *trans*-$[Tc(cyclam)O_2]^+$. Probability ellipsoids are shown at the 50% level. Hydrogen atoms are not included.

Description of the Structure of *trans*-$[Tc(C_{10}H_{24}N4)O_2]ClO_4 \cdot H_2O$. The crystal structure consists of two independent cations per unit cell with their associated anions and lattice

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Table III. Final Positional and Anisotropic Thermal Parameters[a] (with Esd's) for Nonhydrogen Atoms of $[Tc(C_{10}H_{24}N_4)O_2]ClO_4 \cdot H_2O$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tc1	0.00000	0.00000	0.00000	0.0207 (3)	0.0240 (3)	0.0178 (3)	0.0073 (2)	0.0085 (2)	0.0089 (2)
1O1	0.1176 (4)	0.1549 (4)	0.1644 (3)	0.035 (2)	0.034 (2)	0.022 (1)	0.008 (1)	0.010 (1)	0.015 (1)
1N1	0.0469 (4)	−0.1729 (4)	0.0743 (3)	0.032 (2)	0.031 (2)	0.030 (2)	0.013 (2)	0.013 (2)	0.017 (2)
1N2	0.2176 (5)	0.1033 (5)	−0.0195 (4)	0.024 (2)	0.038 (2)	0.031 (2)	0.016 (2)	0.014 (2)	0.012 (2)
1C1	0.1099 (6)	−0.2531 (6)	0.0053 (5)	0.053 (3)	0.039 (3)	0.032 (2)	0.011 (2)	0.018 (2)	0.031 (2)
1C2	0.2724 (6)	−0.1232 (7)	0.0170 (5)	0.038 (3)	0.056 (3)	0.034 (2)	0.015 (2)	0.016 (2)	0.030 (2)
1C3	0.2547 (7)	−0.0228 (7)	−0.0688 (5)	0.037 (3)	0.065 (3)	0.041 (3)	0.023 (3)	0.025 (2)	0.031 (3)
1C4	0.1891 (6)	0.1971 (6)	−0.1073 (5)	0.037 (2)	0.046 (3)	0.044 (3)	0.026 (2)	0.026 (2)	0.013 (2)
1C5	0.1144 (6)	0.2959 (6)	−0.0624 (5)	0.036 (3)	0.033 (2)	0.046 (3)	0.023 (2)	0.018 (2)	0.010 (2)
Tc2	0.50000	1.00000	0.50000	0.0241 (3)	0.0277 (3)	0.0197 (3)	0.0101 (2)	0.0088 (2)	0.0129 (3)
2O1	0.3432 (4)	0.9568 (4)	0.3373 (3)	0.031 (2)	0.042 (2)	0.028 (2)	0.015 (1)	0.011 (1)	0.020 (1)
2N1	0.3996 (5)	1.1214 (5)	0.5815 (4)	0.043 (2)	0.057 (3)	0.032 (2)	0.016 (2)	0.018 (2)	0.036 (2)
2N2	0.6812 (5)	1.2167 (5)	0.4978 (4)	0.033 (2)	0.042 (2)	0.045 (2)	0.027 (2)	0.017 (2)	0.013 (2)
2C1	0.5302 (8)	1.2963 (8)	0.6864 (5)	0.076 (4)	0.067 (4)	0.034 (3)	0.002 (3)	0.015 (3)	0.048 (3)
2C2	0.6278 (8)	1.4046 (7)	0.6315 (7)	0.067 (4)	0.034 (3)	0.069 (4)	0.003 (3)	0.004 (3)	0.028 (3)
2C3	0.7606 (7)	1.3741 (7)	0.6150 (6)	0.045 (3)	0.037 (3)	0.059 (4)	0.018 (3)	0.004 (3)	0.001 (2)
2C4	0.8022 (7)	1.1738 (8)	0.4798 (6)	0.036 (3)	0.082 (4)	0.065 (4)	0.049 (4)	0.031 (3)	0.026 (3)
2C5	0.7037 (9)	0.997 (1)	0.3774 (6)	0.071 (4)	0.134 (7)	0.055 (4)	0.062 (4)	0.051 (4)	0.075 (5)
Cl	0.6854 (1)	0.4239 (1)	0.2518 (1)	0.0358 (6)	0.0392 (6)	0.0390 (7)	0.0131 (5)	0.0151 (5)	0.0155 (5)
O1	0.772 (1)	0.577 (1)	0.354 (1)	0.118 (7)	0.203 (9)	0.20 (1)	−0.135 (8)	−0.021 (7)	0.091 (7)
O2	0.5661 (9)	0.296 (1)	0.2542 (8)	0.099 (5)	0.27 (1)	0.162 (7)	0.179 (8)	−0.024 (5)	−0.059 (6)
O3	0.5966 (9)	0.4280 (8)	0.1287 (6)	0.105 (4)	0.114 (5)	0.100 (4)	0.080 (4)	−0.017 (4)	0.001 (4)
O4	0.800 (1)	0.380 (2)	0.2611 (9)	0.193 (9)	0.31 (1)	0.132 (7)	−0.003 (8)	0.044 (7)	0.21 (1)
O	0.1414 (5)	0.1735 (5)	0.4072 (4)	0.067 (2)	0.065 (2)	0.037 (2)	0.020 (2)	0.018 (2)	0.040 (2)

[a] The form of the expression defining the thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

waters. Each cation has a crystallographically imposed center of symmetry. There are no bonding interactions between cation and anion or water molecules. Both cations consist of a *trans*-$OTcO^+$ moiety complexed by the macrocyclic cyclam ligand which has the trans III set of nitrogen configurations. This is the same set of nitrogen configurations found in four other complexes containing the ligand.[11] A perspective drawing of the cation is given in Figure 1. Bond distances and angles for each cation are given in Table IV. If one allows for the fact that the small differences in the two Tc–N distances that exist in both cations are reversed between the two, then only the C4–C5 and N2–C4 bond distances differ by more than two standard deviations. Since no particular significance can be attached to these differences, discussions of distances and angles which follow will refer only to the values of cation 1 unless otherwise indicated.

Table IV. Selected Interatomic Distances (Å) and Angles (Deg) for the Cation *trans*-Dioxo(cyclam)technetium(V), $[Tc(C_{10}H_{24}N_4)O_2]^+$

	molecule 1	molecule 2
Tc–O	1.749 (3)	1.754 (3)
Tc–N1	2.130 (3)	2.114 (4)
Tc–N2	2.119 (4)	2.139 (4)
N1–C1	1.470 (6)	1.486 (7)
C1–C2	1.526 (7)	1.539 (10)
C2–C3	1.531 (7)	1.534 (10)
C3–N2	1.464 (7)	1.474 (7)
N2–C4	1.512 (6)	1.489 (8)
C4–C5	1.541 (8)	1.485 (10)
C5–N'1	1.500 (5)	1.492 (7)

	molecule 1	molecule 2
N1–Tc–N2	96.2 (1)	96.8 (2)
N1–Tc–O	90.4 (1)	89.7 (1)
N2–Tc–O	90.3 (1)	91.1 (1)
Tc–N1–C1	112.1 (3)	113.6 (3)
Tc–N1–C'5	106.6 (2)	106.5 (2)
Tc–N2–C3	113.4 (3)	112.9 (3)
Tc–N2–C4	106.6 (3)	106.3 (3)
N1–C1–C2	112.1 (4)	110.7 (4)
C1–C2–C3	117.4 (4)	117.5 (5)
C2–C3–N2	112.6 (4)	112.2 (4)
C3–N2–C4	113.6 (4)	115.3 (4)
N2–C4–C5	108.1 (4)	108.8 (4)
C4–C5–N'1	108.4 (4)	110.7 (4)
C5–N'1–C'1	114.1 (3)	115.6 (4)

Discussion

$[Tc(cyclam)O_2]ClO_4 \cdot H_2O$ is one of the first *trans*-dioxotechnetium(V) complexes to be synthesized and is apparently the first to be structurally characterized although the possibility that such complexes should exist could certainly be inferred on the basis of known Re(V) chemistry. There are several points of interest concerning this compound and its structure. The first of these is a comparison of the Tc–O bond distances with those of a number of monooxotechnetium(V) complexes (monooxorhenium analogues are also well-known) and a consideration of the factors that determine the number of oxo groups that are attached to the Tc(V) ion.

The Tc–O distance in the present complex is 1.751 (4) Å (average of values in the two cations) which is 0.1 Å longer than the average value of 1.65 Å found for the Tc–O distance in five monooxo complexes.[12,13] Lengthening of the Tc–O bond distance in the dioxo complex must be a result of competition by the two trans oxygen atoms for the same σ and π orbitals on the metal. In monooxo complexes, the trans ligand is either weakly coordinated or absent entirely; in either case, the single oxygen donor can utilize a greater portion of the metal's σ and π orbitals, and a stronger bond is produced. It should be noted that similar differences in Re–O distances have been observed for monooxo and dioxo complexes. For example, $[Re(en)_2O_2]Cl$ and $[Re(py)_4O_2]Cl \cdot 2H_2O$ have average Re–O distances of 1.765 (7) and 1.764 (13) Å,[14] respectively, whereas

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$(Ph_4As)[ReOCl_4]$ has a Re–O distance of 1.63 (3) Å.[15] The trans dioxo complex $K_3[Re(CN)_4O_2]$ has a slightly longer Re–O distance at 1.781 (3) Å than the complexes with nitrogen bases.[16]

On the basis of information presently available, it appears that dioxo complexes of Tc(V) and Re(V) are formed when the ancillary ligands are neutral and serve as poor π donors, e.g., $[Tc(cyclam)O_2]^+$, $[Tc(py)_4O_2]^+$,[17] $[Re(py)_4O_2]^+$,[14] and $[Re(en)_2O_2]^+$.[14] When the ligands are negatively charged and function as good π donors, five-coordinate monooxo complexes are formed, e.g., $[Tc(SCH_2CH_2S)_2O]^{-1}$,[19] $[Tc[SCH_2C(O)S]_2O]^{-1}$,[6] $ReOCl_4^-$,[15] $TcOCl_4^-$,[13] and the series of oxobis(dithiolate)technetium(V) and -rhenium(V) complexes reported by Davison.[20] None of these monooxo complexes have been converted to a dioxo form, but both $TcOCl_4^-$ and $ReOCl_4^-$[13,15] bind a fifth chloride, and a number of other six-coordinate monooxo complexes are known. It should be noted that none of the monooxo complexes that contain sulfur ligands show any tendency to bind a sixth ligand.[20] $K_3[Tc(CN)_4O_2]$ is a borderline complex since both $TcO(CN)_5^{2-}$ and $[Tc(CN)_4(OCH_3)O]^{2-}$ are known and $[Tc(CN)_4(OH)O]^{2-}$ is apparently formed in very strong acid.[18] These monooxo complexes are unstable in water and convert to the dioxo species.

In summary, the high-charge requirements of a Tc(V) or Re(V) center can be satisfied by one oxo group and four good π-bonding ligands although certain of these compounds may weakly bind a ligand trans to the oxo group. Similar behavior has been observed for both Mo(IV) and Mo(V).[21] If the ligands are only σ donating or are poor π donors, then dioxo species are formed. Mechanistic work on the preparation of these species from TcO_4^- is lacking so that it is not known how the *trans*-dioxotechnetium(V) complexes are formed; however, Davison has shown that $[Tc(py)_4O_2]^+$ can be generated from $TcOCl_4^-$ with pyridine in aqueous solution.[17] This must mean that water coordinated trans to the oxo group is sufficiently acidic so that the second oxo group is formed by double deprotonation and that this is a direct result of the Tc(V) center's high-charge requirements that are poorly satisfied by the σ-donating pyridine ligands.

A second point of interest concerns the structure of the cyclam ligand. The Tc–N distances of 2.125 (11) Å (average of distances in both molecules) are the longest observed for any cyclam complex to date.[11] The distances in the four other structures are as follows: Ni(II), 2.065 (2); Cu(II), 2.02 (4); Co(II), 1.980 (4); Ni(III), 1.968 (5) Å. Conformational analysis studies of saturated macrocyclic tetraamine ligands and their metal complexes suggested that ligand strain energy would be minimized for M–N distances of about 2.07 Å in the case of cyclam.[22] Although there is clearly some uncertainty about the ideal distance, the Tc complex might be expected to show some structural effects of strain introduced because of the long metal–donor distances.

As previously stated, the gross structural features are the same as those in other complexes and the average C–C and C–N bond distances are identical, but there are small differences in interatomic and torsion angles in the cyclam ligand that do suggest there is some strain associated with the long Tc–N bond distance. A complete comparison of structural parameters for all five cyclam complexes will be reserved for a future paper,[23] but a few comparisons of the Tc parameters with those of the Ni(III) complex will be given to indicate the magnitude of the differences. In the six-membered chelate ring, the increased M–N distance is accommodated by an opening up of the C1–C2–C3 angle in the Tc complex (by 4°) and an increased "puckering" of the N1–C1–C2–C3–N2 unit. This puckering is reflected in the N1–C1–C2–C3 and C1–C2–C3–N2 torsion angles (74 and 72°, respectively) which are 7 and 6°, respectively, larger than those in the Ni(III) complex. The longer M–N bonds in the five-membered chelate ring of the Tc complex are accommodated by a decreased N1–Tc–N′2 angle (2.1°) and an increased N2–C4–C5–N′1 torsion angle (58° compared to 54°).

None of the structural features in the Tc–cyclam complex that are attributable to strain effects appear to be particularly severe. This raises the interesting question of how much larger a metal ion can be and still fit into a planar 14-membered tetraaza ligand. Pt(II) would seem to be a promising candidate for such a study since numerous planar, four-coordinate complexes are known.

Future work in the area of Tc–macrocyclic ligand chemistry will explore the chemistry and structural features of complexes that contain uninegative macrocyclic ligands and cyclam ligands that are functionalized with one or more potential donor groups. The reactivity and stability of the trans dioxo function in these environs will receive special attention.

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Supplementary Material Available: Listings of positional and isotropic thermal parameters for hydrogen atoms and the observed and calculated structure factors for *trans*-$[Tc(C_{10}H_{24}N_4)O_2]ClO_4\cdot H_2O$ (13 pages). Ordering information is given on any current masthead page.

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