Atomic coordinates and isotropic equivalent thermal parameters are collected in Table VI.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table VII), complete bond distances (Table VIII) and angles (Table IX), and hydrogen atom positional parameters (Table X) and a structure determination summary (Table XI) (5 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Neutral, Seven-Coordinate Dioxime Complexes of Technetium(III): Synthesis and Characterization

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The tin-capped complexes ^{99}Tc(oxime)$_3$(μ-OH)SnCl$_3$ [oxime = dimethylglyoxime (DMG) or cyclohexanedione dioxime (CDO)] can be prepared by the reduction of NH$_4$TcO$_4$ with 2 equiv of SnCl$_2$ in the presence of dioxime and HCl. These tin-capped complexes can be readily converted into a new class of uncapped Tc–dioxime compounds, TcCl(oxime)$_3$, by treatment with HCl. This reaction is reversible. Both the tin-capped and uncapped tris(dioxime) complexes can be converted to the previously reported boron-capped Tc–dioxime complexes TcCl(oxime)$_3$BR (R = alkyl, OH) by reaction with boronic acids or with boric acid at low pH. All of these complexes [Tc(oxime)$_3$(μ-OH)SnCl$_3$, TcCl(oxime)$_3$, and TcCl(oxime)$_3$BR] appear to be neutral, seven-coordinate compounds of technetium(III). They have been characterized by elemental analysis, ^{1}H NMR and UV/visible spectroscopy, conductivity, and fast atom bombardment mass spectrometry. The synthesis, characterization, and reactivity of these compounds is discussed. The X-ray crystal structure analysis of TcCl(DMG)$_3$ and an abbreviated structure report on TcCl(DMG)$_3$MeB are described. Crystal data for TcCl(DMG)$_3$: a = 9.617 (1) Å, b = 12.135 (3) Å, c = 9.244 (2) Å, α = 110.24 (2)°, β = 92.36 (2)°, γ = 88.92 (2)°, space group = $P\bar{1}$, Z = 2. Final R = 0.041; R_w = 0.047. Data for TcCl(DMG)$_3$MeB: a = 20.290 (3) Å, b = 14.468 (2) Å, c = 16.404 (3) Å, β = 124.65 (1)°, space group = $C2/c$, Z = 8. Final R = 0.039; R_w = 0.044.

Introduction

We have recently prepared[1] a large number of neutral, seven-coordinate technetium(III) dioxime complexes, TcX(oxime)$_3$BR (X = halogen, R = alkyl, OH), which are capped at one end through three dioxime oxygens by a tetravalent boron atom. This BATO (boronic acid adducts of technetium dioximes) class of complexes (Figure 1) can be prepared by SnCl$_2$ reduction of ^{99}TcO$_4^-$ in the presence of vicinal dioximes and a boronic acid. Our interest in these complexes stems from the fact that several of them exhibit myocardial[2] or brain[3] uptake, when prepared with the short-lived, γ-emitting nuclide, ^{99m}Tc. Two compounds in this class, TcCl(CDO)$_3$MeB and TcCl(DMG)$_3$(2MP), are currently in clinical trials as agents for imaging heart and brain perfusion. (CDO = cyclohexanedione dioxime, DMG = dimethylglyoxime, MeB = methylboron, 2MP = (2-methyl-1-propyl)boron.)

These BATO complexes form via template synthesis.[4] To better understand how these complexes are formed from ^{99}TcO$_4^-$, we have examined this reaction in detail. We report here the synthesis and characterization of two dioxime-containing intermediates that are precursors to the BATO compounds, Tc(oxime)$_3$(μ-OH)SnCl$_3$ and TcCl(oxime)$_3$ (oxime = DMG, CDO).

The complex Tc(DMG)$_3$(μ-OH)SnCl$_3$ was first prepared by Deutsch et al.,[5] using a modification of an analytical procedure[6] for the detection of technetium. Addition of excess chlorostannic acid to an acidic mixture of TcO$_4^-$ and DMG yields a deep green solution. Deutsch et al. allowed this green solution to go to near dryness over several weeks and isolated yellow crystals from the reaction mixture in low yield. The preparation was not reproducible; therefore, only the X-ray crystal structure analysis[5] of the complex was reported. Libson[7] later found that H$_2$O$_2$ could oxidize the green precursor to the desired yellow complex in solution and reported the UV/visible spectra of the DMG complex

Table I. Crystallographic Parameters for TcCl(DMG)$_3$

formula	TcC$_{12}$H$_{22}$N$_6$ClO$_6$·0.5CH$_2$Cl$_2$
fw	523.27
space group	$P\bar{1}$
a, Å	9.617 (1)
b, Å	12.135 (3)
c, Å	9.244 (2)
α, deg	110.24 (2)
β, deg	92.36 (2)
γ, deg	88.92 (2)
V, Å^3	1011.3 (8)
Z	2
D_{calc}, g/cm^3	1.72
D_{obs}(flotation), g/cm^3	1.74
cryst size, mm	0.25 × 0.15 × 0.25
μ, cm^{-1}	10.0
transm factor	0.87–1.00
scan method	θ–2θ
scan range (2θ), deg	0–50
no. of reflcns measd	4999
no. of indep reflcns	4672
no. of data with $F_o^2 \geq 3\sigma$	3350
no. of refined variables	253
R	0.041
R_w	0.047

and its CDO analogue. We have developed an improved synthesis of these yellow tin-capped compounds and have found them to

(1) (a) Treher, E. N.; Gougoutas, J.; Malley, M.; Nunn, A. D.; Unger, S. E. *J. Labelled Compd. Radiopharm.* **1986**, *23*, 1118. (b) Unger, S. E.; McCormick, T. J.; Treher, E. N.; Nunn, A. D. *Anal. Chem.* **1987**, *59*, 1145. (c) Treher, E. N.; Francesconi, L. C.; Gougoutas, J. Z.; Malley, M. F.; Nunn, A. D. *Inorg. Chem.* **1989**, *28*, 3411.

(2) (a) Coleman, R. E.; Maturi, M.; Nunn, A. D.; Eckelman, W.; Juri, P. N.; Cobb, F. R. *J. Nucl. Med.* **1986**, *27*, 893. (b) Narra, R. K.; Feld, T.; Wedeking, P.; Nunn, A. D. In *Nuklearmedizin: Clinical Demands on Nuclear Chemistry*; Schmidt, H. A. E., Emrich, D., Eds.; F. K. Schattauer Verlag: New York, 1987; p 489. (c) Seldin, D. W.; Johnson, L. L.; Blood, D. K.; Muschel, M. J.; Smith, K. F.; Wall, R. M.; Cannon, P. J. *J. Nucl. Med.* **1989**, *30*, 312.

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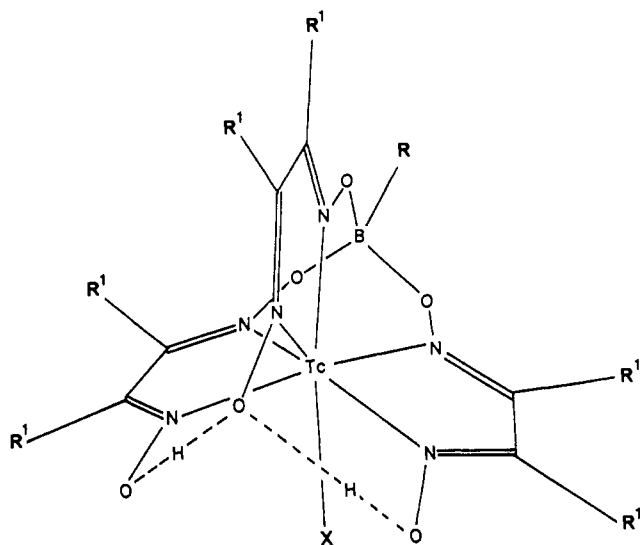†Present address: Department of Drug Metabolism, Glaxo Inc., Research Triangle Park, NC 27709.

Figure 1. General structure of the BATO Complexes TcX(oxime)₃BR.

be useful starting materials for the synthesis of other dioxime-containing Tc complexes. Originally, the oxidation state of these complexes was tentatively reported as Tc(V).[5a] We now present evidence that they may be complexes of Tc(III).

Experimental Section

Ammonium pertechnetate (NH₄TcO₄) from Oak Ridge National Laboratories was recrystallized from dilute aqueous H_2O_2. ^{99}Tc is a weak β-emitter (0.29 MeV, half-life 2.12×10^5 years); therefore, all manipulations were carried out in laboratories approved for the use of low-level radioactivity. Dimethylglyoxime (Eastern Chemicals) and cyclohexanedione dioxime (Fluka) were recrystallized from aqueous ethanol. All other chemicals were of reagent grade and were used as received.

Absorption spectra were recorded with a Hewlett-Packard 8451A photodiode-array spectrophotometer. Proton NMR spectra were obtained on a JEOL GX-270 spectrometer, using TMS as an internal standard. Fast atom bombardment (FAB) mass spectra were obtained on a VG-ZAB-2F instrument (Vacuum Generators, Ltd., Altringham, Great Britain), as described previously.[1b] Conductivity measurements in acetonitrile (ACN) were performed with a Yellow Springs Model 32 conductivity meter. Elemental analyses were performed by the Squibb Microanalytical Department.

Crystallography. X-ray data were collected on a Syntex P2₁ diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Crystal data and some details of the structure refinement for TcCl(DMG)₃ are given in Table I; atomic coordinates are given in Table II. Details of the crystallographic characterization of TcCl(DMG)₃MeB are given as supplementary material, as the structure of this complex is similar to that of previously reported BATO compounds.[1c] For each compound, Weissenberg and precession films were used to confirm the space group assignment. The unit cell parameters were obtained through a least-squares analysis of the experimental diffractometer settings of 15 high-angle reflections. Crystal densities were measured by flotation in carbon tetrachloride/bromoform mixtures. Crystals for data collection were coated with epoxy cement. Reflections were measured at 23 °C with the θ–2θ variable-scan technique and were corrected for Lorentz polarization factors and for absorption by the DIFABS[8a] procedure. Background counts were collected at the extremes of the scan for half

(3) (a) Linder, K. E.; Feld, T.; Juri, P. N.; Nunn, A. D.; Treher, E. N. *J. Nucl. Med.* **1987**, *28*, 592. (b) Kuczynski, B. L.; Silva, D.; Feld, T.; Ita, C.; Narra, R. K.; Nunn, A. D.; Eckelman, W. C.; Coleman, R. E. *J. Nucl. Med.* **1987**, *28*, 1081.
(4) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley and Sons: New York, 1980; p 80 and references therein.
(5) (a) Deutsch, E.; Elder, R. C.; Lange, B. A.; Vaal, M. J.; Lay, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 4289. (b) Bandolini, G.; Mazzi, U.; Roncari, E.; Deutsch, E. *Coord. Chem. Rev.* **1982**, 44.
(6) Jasim, F.; Magee, R. J.; Wilson, C. L. *Talanta* **1959**, *2*, 93.
(7) Libson, K. Ph.D. Thesis, University of Cincinnati, 1981, 130.
(8) (a) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 159. (b) SDP. Structure Determination Package. A. Frenz and Associates, College Station, TX. (c) Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table II. Final Positional Parameters for TcCl(DMG)₃

atom	x	y	z
Cl′	0.3777 (3)	0.9405 (2)	0.0171 (3)
C′	0.484 (2)	1.058 (1)	0.091 (1)
Tc	0.77472 (4)	0.72166 (3)	0.34541 (4)
Cl	0.6402 (1)	0.7492 (1)	0.5698 (1)
N1F	0.7275 (4)	0.9028 (3)	0.4036 (4)
N1B	0.9181 (4)	0.8197 (3)	0.5213 (4)
N2F	0.5895 (4)	0.6323 (3)	0.2357 (4)
N2B	0.7838 (4)	0.5468 (3)	0.3463 (4)
N3F	0.7751 (4)	0.7416 (3)	0.1305 (4)
N3B	0.9658 (4)	0.6638 (3)	0.2459 (4)
O1F	0.6242 (4)	0.9490 (3)	0.3324 (4)
O1B	1.0258 (4)	0.7707 (3)	0.5827 (4)
O2F	0.4838 (3)	0.6822 (3)	0.1733 (4)
O2B	0.8940 (3)	0.4971 (3)	0.4009 (4)
O3F	0.6625 (3)	0.7873 (3)	0.0792 (4)
O3B	1.0634 (3)	0.6196 (3)	0.3204 (4)
C11	0.7322 (6)	1.1029 (5)	0.5958 (7)
C12	0.7804 (5)	0.9786 (4)	0.5294 (5)
C13	0.8917 (5)	0.9290 (4)	0.5980 (5)
C14	0.9706 (6)	0.9983 (5)	0.7436 (6)
C21	0.4174 (5)	0.4806 (5)	0.2141 (7)
C22	0.5580 (5)	0.5346 (4)	0.2528 (5)
C23	0.6719 (5)	0.4823 (4)	0.3143 (5)
C24	0.6664 (6)	0.3655 (4)	0.3315 (7)
C31	0.8866 (6)	0.7324 (5)	-0.1085 (5)
C32	0.8831 (5)	0.7147 (4)	0.0437 (5)
C33	0.9961 (5)	0.6688 (4)	0.1114 (5)
C34	1.1313 (5)	0.6290 (5)	0.0395 (6)
H1F	0.639	0.889	0.221
H2F	0.527	0.750	0.139
H2B	0.971	0.527	0.359
H1B	1.057	0.695	0.473

of the time of the scan. Two standard reflections were monitored for decay every 50 reflections; no decrease of intensity was observed during the course of the measurements. Structures were solved by standard heavy-atom techniques and refined on the basis of "observed" reflections with $I \geq 3\sigma(I)$. All calculations utilized the SDP program package with minor local modifications.[8b] The least-squares weights $w = \sigma^{-2}(F_o)$ were calculated with the assumption that $\sigma^2 = \epsilon^2 + (pI)^2$ where ϵ is the statistical counting error and $p = 0.04$. The function minimized in the least-squares refinements was $\sum w(|F_o| - |F_c|)^2$. R is defined as $\sum ||F_o| - |F_c||/\sum |F_o|$ while R_w is defined as $[\sum w(|F_o| - |F_c|)^2]/[\sum w(F_o)^2]^{1/2}$. In both structures, all hydroxyl hydrogen atoms were introduced at positions observed in difference maps. Although most of the methyl hydrogens were also evident, all were introduced at idealized positions consistent with the difference peaks. All hydrogen atoms were included in structure factor calculations, but their coordinates were not refined. Refined variables for TcCl(DMG)₃MeB were the coordinates and anisotropic temperature factors of all non-hydrogen atoms.

Analysis of TcCl(DMG)₃, assuming space group P1̄, clearly revealed all of the non-hydrogen atoms of one complex in the asymmetric unit. Refinements of the coordinates and isotropic temperature factors converged to $R = 0.12$. Difference maps at this stage revealed two other (centrosymmetrically related) chlorine atoms (Cl--Cl = 2.9 Å) in the unit cell, in accord with the elemental analysis data, which suggest a 1:2 molar ratio of CH_2Cl_2 to complex. The carbon atom of CH_2Cl_2 was introduced in the observed, off-center position with 0.5 multiplicity, since the solvent must be site disordered in this space group. Least-squares refinements of all coordinates and anisotropic temperature factors for the non-hydrogen atoms converged at $R = 0.04$. Refinements of a fully ordered structure in the lower symmetry space group P1 did not give significantly better results. The complex has C_{2v} symmetry within experimental error, but none of the molecular symmetry elements are compatible with the triclinic lattice metric. Tables of thermal parameters, structure factors, bond distances and bond angles, and atomic positional parameters for both TcCl(DMG)₃ and TcCl(DMG)₃MeB are included as supplemental material.

Tc(DMG)₃(μ-OH)SnCl₃·xH₂O from TcO₄⁻. To a stirred solution of DMG (362 mg, 3.17 mmol) in 40 mL of EtOH was added NH₄TcO₄ (174 mg, 0.96 mmol) dissolved in 10 mL of 0.5 M HCl. A freshly prepared solution of SnCl₂ (363 mg, 1.92 mmol), dissolved in 8 drops of concentrated HCl and 3 mL of H₂O, was added dropwise, with stirring, over 5 min. The resultant red-brown solution was stirred at room temperature for 30 min and then heated at a gentle boil to remove ethanol until precipitation of product began. (Note: prolonged heating causes decomposition.) The yellow-brown mixture was then cooled to room

temperature, and 20 mL of 1 M HCl was added. The yellow-orange precipitate was isolated by filtration on a medium-fritted funnel, washed with 1 M HCl and dried in vacuo for 24 h. Crude yield: 380 mg, 52%. For recrystallization, Tc(DMG)$_3$(μ-OH)SnCl$_3$ was dissolved in a minimal volume of boiling methanol. A solution of 3 M HCl (0.5 mL) containing 50 mg of SnCl$_2$ was added dropwise, with stirring. A microcrystalline yellow-orange solid formed rapidly and was isolated as above, after the solution was chilled to 0 °C. The product, when vacuum-dried for 48 h, was isolated as a monohydrate. If dried over P$_2$O$_5$, the trihydrate reported by Deutsch[5] was isolated. The UV/visible spectrum of this material is in agreement with that reported by Libson.[7] Overall yield: 233 mg, 32%. Anal. Calcd for Tc(DMG)$_3$(μ-OH)SnCl$_3$·H$_2$O (C$_{12}$H$_{24}$N$_6$Cl$_3$O$_8$SnTc): C, 20.46; H, 3.43; N, 11.93. Found: C, 20.52; H, 3.20; N, 11.91. Conductivity (ACN): 7.7 Ω^{-1} M^{-1} cm^2.

Tc(CDO)$_3$(μ-OH)SnCl$_3$·3H$_2$O from TcO$_4^-$. NH$_4$TcO$_4$ (116 mg, 0.64 mmol) in 4 mL of water was added, with stirring, to a solution of CDO (295 mg, 2.1 mmol) in 30 mL of ethanol. Four milliliters of 4 M HCl was added, followed immediately by a solution of SnCl$_2$ (243 mg, 1.28 mmol) in 5 drops of concentrated HCl and 3 mL of H$_2$O. The resultant deep red-brown solution was stirred for 1 h. During this time, the precipitation of yellow-orange product began. The solution was then reduced to 20 mL by gentle boiling and cooled to room temperature, and 50 mL of 1 M HCl was added. (Cautionary note: The reaction mixture must be heated gently, with vigorous stirring, to prevent "bumping".) The precipitate was isolated by suction filtration, washed with 10 mL of 1M HCl, and dried in vacuo at room temperature for at least 24 h. (Crude yield: 444 mg, 86%.) The dried crude product was recrystallized by dissolution in 10 mL of ACN, followed by the rapid addition of 20 mL of 0.5 M HCl that contained 50 mg of SnCl$_2$. The product precipitated from solution immediately and was isolated as above. Overall yield: 330 mg (64%). Anal. Calcd for Tc(CDO)$_3$(μ-OH)SnCl$_3$·3H$_2$O (C$_{18}$H$_{34}$N$_6$Cl$_3$O$_{10}$SnTc): C, 26.41; H, 4.19; N, 10.27. Found: C, 26.45; H, 4.24; N, 10.21. The UV/visible spectrum of this complex is in agreement with that reported by Libson.[7] Conductivity (ACN): 7.2 Ω^{-1} M^{-1} cm^2.

TcCl(DMG)$_3$ from Tc(DMG)$_3$(μ-OH)SnCl$_3$. The complex Tc-(DMG)$_3$(μ-OH)SnCl$_3$·H$_2$O (243 mg, 0.345 mmol) was partially dissolved in 5 mL of ACN. Five drops of concentrated HCl were added with stirring and the solution was allowed to stand at room temperature (without stirring) for 30 min. During this time, starting material dissolved, the color of the solution changed to deep red-orange, and crystals of TcCl(DMG)$_3$ began to form. The solution was chilled to −20 °C to complete crystallization. The supernate was removed, and the crystals were washed quickly with 2 × 1 mL of ice-cold ACN and 5 mL of 1 M HCl and dried in vacuo for 6 h. Crude yield: 136 mg, 82%. Needles were obtained by rapid cooling of a boiling ethanolic HCl solution of the complex. Anal. Calcd for C$_{12}$H$_{22}$N$_6$ClO$_6$Tc: C, 29.97; H, 4.61; N, 17.48. Found: C, 30.12; H, 4.60; N, 17.46.

Crystals for the X-ray structure determination were grown from CH$_2$Cl$_2$/hexanes, and contained 0.5 molecule of CH$_2$Cl$_2$ per TcCl-(DMG)$_3$ when dried in air. After vacuum drying, 0.25 CH$_2$Cl$_2$ per Tc was found. Anal. Calcd for C$_{12}$H$_{22}$N$_6$ClO$_6$Tc·0.25CH$_2$Cl$_2$: C, 29.31; H, 4.52; N, 16.73. Found: C, 29.29; H, 4.42; N, 16.58. Conductivity (ACN/H$_2$O 1:1): 1.15 Ω^{-1} M^{-1} cm^2.

TcCl(CDO)$_3$ from Tc(CDO)$_3$(μ-OH)SnCl$_3$. The complex Tc-(CDO)$_3$(μ-OH)SnCl$_3$·3H$_2$O (195 mg, 0.24 mmol) was dissolved in 10 mL of ACN and 5 drops of concentrated HCl was added with stirring. The color of the solution changed rapidly to bright red-orange. After 30 min, 10 mL of cold 1 M HCl was added. The resulting red-orange precipitate was isolated within 15 min, washed with 10 mL of 1 N HCl and H$_2$O, and dried in vacuo. Crude yield: 100 mg, 75%. Analytically pure product was obtained by the addition of cold 1 M HCl to a concentrated ACN solution of the complex. Anal. Calcd for C$_{18}$H$_{28}$N$_6$ClO$_6$Tc: C, 38.68; H, 5.05; N, 15.04. Found: C, 38.56; H, 5.01; N, 14.84. Conductivity (ACN): 1.5 Ω^{-1} M^{-1} cm^2.

TcCl(CDO)$_3$ from NH$_4$TcO$_4$. Triphenylphosphine (440 mg, 3.2 mmol) was added to a stirred solution of NH$_4$TcO$_4$ (98 mg, 0.54 mmol) and CDO (386 mg, 2.72 mmol) in 30 mL of EtOH and 15 mL of 1 M HCl. The solution was heated at 50 °C for 1 h and then cooled to room temperature. Water (25 mL) was added, and the product was extracted into 30 mL of CH$_2$Cl$_2$. After being washed with water, the organic phase was dried over Na$_2$SO$_4$, filtered, and reduced to 5 mL by rotary evaporation. The product was purified by silica gel chromatography on a 1.5 × 20 cm column that was conditioned and eluted with CH$_2$Cl$_2$/ACN (9:1). The first orange band was collected and evaporated to dryness. After recrystallization from ACN/HCl, the product thus isolated (75 mg, 24% yield) was indistinguishable from that prepared above, as determined by HPLC, TLC, and UV/visible spectroscopy.

Tc(CDO)$_3$(μ-OH)SnCl$_3$ from TcCl(CDO)$_3$. A solution of SnCl$_4$·5H$_2$O (90 mg, 0.26 mmol) in 10 mL of EtOH was added to a solution of

TcCl(CDO)$_3$ (72 mg, 0.129 mmol) in 20 mL of EtOH. After 1 h, 0.2 M HCl (20 mL) was added and the volume of the solution was reduced to 25 mL by boiling gently. On cooling, an orange precipitate formed. This was isolated by filtration, washed with 0.2 M HCl and dried in vacuo for 24 h to yield 0.127 mmol of Tc(CDO)$_3$(μ-OH)SnCl$_3$ (102 mg, 97%). After recrystallization from ACN/0.5 M HCl, the product was indistinguishable from that prepared by SnCl$_2$ reduction of TcO$_4^-$, as determined by UV/vis spectroscopy, TLC, and elemental analysis.

TcCl(DMG)$_3$BOH from TcCl(DMG)$_3$. A solution of boric acid (9.5 mg, 0.15 mmol) in 1 mL of 2 M HCl, was added to TcCl(DMG)$_3$ (69 mg, 0.14 mmol) in 5 mL of ACN. The solution was heated for 15 min at 60 °C and then evaporated to dryness. The resulting orange solid was dissolved in 2 mL of CH$_2$Cl$_2$ and flash chromatographed on a 230–400 mesh silica gel column (1.5 × 6 cm), which was conditioned with CH$_2$Cl$_2$ and eluted with 60/40 CH$_2$Cl$_2$/ACN. The product eluted as a deep red band and was evaporated to dryness to yield 72 mg of TcCl(DMG)$_3$BOH (95% yield), isolated as the monohydrate. Anal. Calcd for C$_{12}$H$_{21}$N$_6$BClO$_8$Tc: C, 27.40; H, 3.95; N, 15.85. Found: C, 27.47; H, 4.03; N, 16.02.

TcCl(DMG)$_3$MeB from TcCl(DMG)$_3$. By use of the procedure above, but with methylboronic acid substituted for boric acid, the complex TcCl(DMG)$_3$MeB was isolated in 94% yield. The product was identical with that prepared as described below.

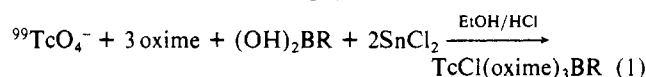**TcCl(DMG)$_3$MeB from NH$_4$TcO$_4$.** A solution of DMG (641 mg, 5.52 mmol) and methylboronic acid (250 mg, 4.2 mmol) in 50 mL of EtOH was added to NH$_4$TcO$_4$ (250 mg, 1.38 mmol) in 15 mL of 1 M HCl. A solution of SnCl$_2$ (523 mg, 2.76 mmol) dissolved in 1 mL of concentrated HCl and 3 mL of H$_2$O was added dropwise, with stirring. The resulting red-brown solution was stirred for 30 min and then heated at a gentle boil to reduce the volume of solvent until precipitation of product began. The solution was cooled to room temperature, and an equal volume of 0.5 M HCl was added. The product was isolated by suction filtration, washed with 1 M HCl and water, and dried in vacuo for 6 h to yield 400 mg (51%) of crude product. Recrystallization from 30 mL of warm ACN and 20 mL of 0.2 M HCl yielded analytically pure product on slow cooling. Anal. Calcd for C$_{13}$H$_{23}$N$_6$BClO$_6$Tc: C, 30.94; H, 4.59; N, 16.65. Found: C, 31.21; H, 4.64; N, 16.78. Conductivity (ACN): 2.3 Ω^{-1} M^{-1} cm^2. Crystals for the X-ray structure determination were grown by slow evaporation of a 1:1 CH$_2$Cl$_2$/hexanes solution at room temperature.

TcCl(CDO)$_3$MeB from Tc(CDO)$_3$(μ-OH)SnCl$_3$. To Tc(CDO)$_3$(μ-OH)SnCl$_3$·3H$_2$O (77 mg, 0.094 mmol) and methylboronic acid (18 mg, 0.25 mmol) dissolved in 10 mL of ACN was added 3 mL of 3 M HCl, with stirring. The solution was heated at 50 °C for 45 min and then cooled to room temperature, and an equal volume of 1M HCl was added. The red-orange precipitate (49 mg, 87%) was isolated by filtration, washed with 1 M HCl and H$_2$O, and dried in vacuo. Recrystallization from 10 mL of ACN/1 M HCl (1:1) yielded analytically pure needles. Anal. Calcd for C$_{19}$H$_{29}$N$_6$BClO$_6$Tc: C, 39.16; H, 5.02; N, 14.42. Found: C, 39.12; H, 5.10; N, 14.31. Conductivity (ACN): 1.5 Ω^{-1} M^{-1} cm^2.

TcCl(CDO)$_3$MeB from TcCl(CDO)$_3$. TcCl(CDO)$_3$ (106 mg, 0.19 mmol) and methylboronic acid (12 mg, 0.2 mmol) were heated at 50 °C in 10 mL of ACN and 1 mL of 3 M HCl for 30 min. After cooling, 10 mL of 1 M HCl was added. The resulting analytically pure precipitate (105 mg, 95%) was isolated as described above.
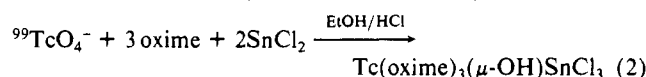
Results and Discussion

Synthesis. As reported previously,[1] the BATO (boronic acid adducts of technetium dioximes) class of complexes can be prepared via reduction of ^{99}TcO$_4^-$ by SnCl$_2$ in the presence of vicinal dioximes and boronic acid (eq 1). As we will show below, the

$$^{99}\text{TcO}_4^- + 3\,\text{oxime} + (\text{OH})_2\text{BR} + 2\text{SnCl}_2 \xrightarrow{\text{EtOH/HCl}} \text{TcCl(oxime)}_3\text{BR} \quad (1)$$

formation of these BATO compounds from ^{99}TcO$_4^-$ proceeds through several intermediates, two of which appear to be neutral dioxime complexes of technetium(III).

If the boronic acid is omitted from eq 1 above, the major products isolated from the reaction mixture (eq 2) are the tin-capped dioxime complexes (Figure 2) previously described by Deutsch[5] and Libson[7] (oxime = DMG, CDO).

$$^{99}\text{TcO}_4^- + 3\,\text{oxime} + 2\text{SnCl}_2 \xrightarrow{\text{EtOH/HCl}} \text{Tc(oxime)}_3(\mu\text{-OH})\text{SnCl}_3 \quad (2)$$

In the previously reported syntheses of these complexes, a large excess of SnCl$_2$ was used, and the complexes Tc(DMG)$_3$(μ-

Figure 2. Structure of Tc(DMG)₃(μ-OH)SnCl₃.
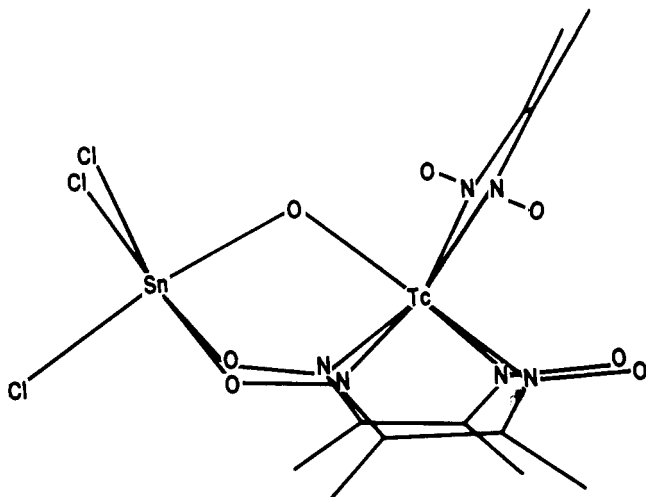

Figure 3. Structure of TcCl(DMG)₃.

OH)SnCl₃ or Tc(CDO)₃(μ-OH)SnCl₃ were formed only after oxidation of the reaction mixture with air[5] or peroxide.[7] The syntheses reported here use only 2 equiv of tin and proceed to completion even in the absence of air. The compounds also form if 1 equiv of $SnCl_2$ is used; however, the isolated yields are considerably lower.

These tin-capped complexes are stable to air but they are relatively unstable in the absence of Sn(IV). The complexes are moderately soluble in ACN, acetone, and warm alcohol but only sparingly soluble in H_2O or nonpolar solvents. They are neutral, as determined by conductivity measurements in ACN. Measurements must be made immediately after dissolution, as the conductance of the solutions rises steadily with time.

TcCl(oxime)₃. The addition of HCl to a solution of Tc(oxime)₃(μ-OH)SnCl₃ in ACN causes loss of the tin cap and formation of the Tc(III) complexes TcCl(oxime)₃ (eq 3). Acid is

$$\text{Tc(oxime)}_3(\mu\text{-OH})\text{SnCl}_3 \xrightarrow{\text{ACN/HCl}} \text{TcCl(oxime)}_3 + \text{SnCl}_4$$

$$(3)$$
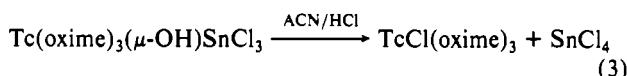
required for this decomposition; if NaCl is substituted for HCl, no reaction occurs. The complexes TcCl(oxime)₃ (oxime = DMG, CDO) are freely soluble in CH_2Cl_2 and $CHCl_3$ and are insoluble in water or hexane. Conductivity measurements indicate that they are neutral. The formation of TcCl(oxime)₃ from Tc(oxime)₃(μ-OH)SnCl₃ is inhibited by the presence of excess $SnCl_4$. Presumably, this is because TcCl(oxime)₃ can react with $SnCl_4$ and H_2O to re-form Tc(oxime)₃(μ-OH)SnCl₃. The preparation of Tc(CDO)₃(μ-OH)SnCl₃ in 97% yield by reaction of TcCl(CDO)₃ and $SnCl_4$ demonstrates this back reaction quite clearly (eq 4). We have found that TcCl(oxime)₃ cannot be prepared in high

$$\text{TcCl(oxime)}_3 + \text{SnCl}_4 \xrightarrow{\text{EtOH/H}_2\text{O}} \text{Tc(oxime)}_3(\mu\text{-OH})\text{SnCl}_3$$

$$(4)$$
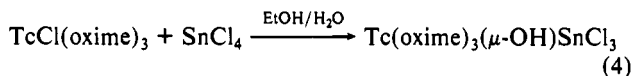
yield from ⁹⁹TcO₄⁻ if $SnCl_2$ is used as the reductant; Tc(oxime)₃(μ-OH)SnCl₃ is the major product formed. However, the TcCl(oxime)₃ complexes can be formed from TcO₄⁻ if triphenylphosphine is used as the reductant. Overall yield in this reaction is low, due to the formation of phosphine-containing side products.

The ¹H NMR spectrum of TcCl(DMG)₃ indicates that the solution geometry of this complex (Figure 3) is the same as that noted in the crystal structure analysis (vide infra). All four methyl groups on the two equivalent DMG ligands are magnetically equivalent and fall as a singlet (12 H) at 2.38 ppm. The two methyl groups in the unique DMG ligand are also equivalent, falling as a singlet (6 H) at 2.42 ppm. The four hydrogen-bonded oxime protons are seen as a broad singlet (4 H) at 15.3 ppm. This chemical shift is characteristic of protons that are shared between
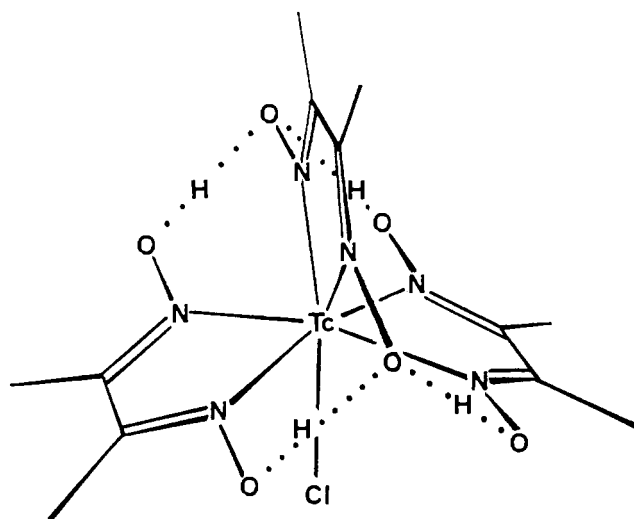

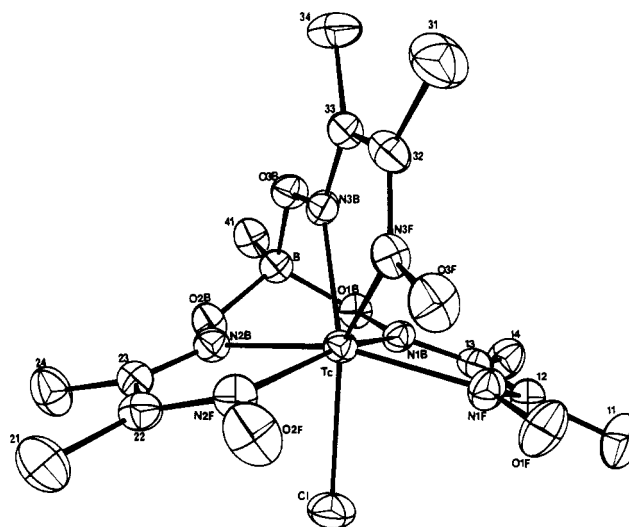**Figure 4.** ORTEP diagram of TcCl(DMG)₃MeB, showing the atom-numbering scheme and 50% probability ellipsoids.

two oxime oxygens O··H··O.[9] The corresponding oxime protons in the ¹H NMR spectrum of TcCl(CDO)₃ fall at 15.15 ppm (4 H). All of the oxime OH protons undergo deuterium exchange when treated with D_2O.

The TcCl(oxime)₃ complexes give a strong protonated molecular ion under positive FAB conditions. The molecular weight observed for the (M + H)⁺ ion indicates that the compounds contain the four protons that were observed in the ¹H NMR spectra, as expected for these Tc(III) complexes.

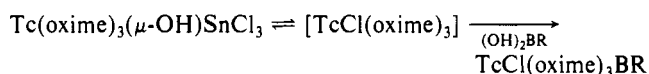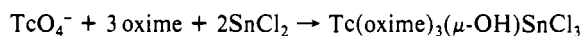**Formation of BATO Complexes.** Both TcCl(CDO)₃ and TcCl(DMG)₃ react rapidly with boronic acid to form the Tc(III) BATO complexes TcCl(oxime)₃BR in close to quantitative yield. Even if excess boronic acid is used, only the monocapped complex forms. We have seen no indication of the formation of bis capped products in these reaction mixtures.[1,10] This is in contrast to the ready formation of biscapped species M(oxime)₃(BR)₂ (M = Fe, Co, or Ru).[11] The tin-capped complexes Tc(oxime)₃(μ-OH)SnCl₃ also react with boronic acids to yield the boron-capped BATO complexes. However, TcCl(oxime)₃ is noted (by TLC and HPLC)

(9) Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1 and references therein.
(10) Jurisson, S.; Francesconi, L.; Juri, P.; Linder, K.; Treher, E.; Gougoutas, J.; Malley, M.; Nunn, A. D. *J. Labelled Compd. Radiopharm.* **1989**, *26*, 27.
(11) (a) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 4163. (b) Johnson, J. N.; Rose, N. J. *Inorg. Synth.* **1982**, *21*, 112. (c) Jackels, S. C.; Rose, N. J. *Inorg. Chem.* **1973**, *12*, 1232. (d) Muller, J. G.; Grzybowski, J. J.; Takeuchi, K. J. *Inorg. Chem.* **1986**, *25*, 2665.

Table III. Selected Bond Distances (Å) for TcCl(DMG)₃MeB and TcCl(DMG)₃

	TcCl(DMG)₃MeB	TcCl(DMG)₃
Tc–Cl	2.415 (1)	2.411 (1)
Tc–N1F	2.120 (5)	2.120 (4)
Tc–N1B	2.047 (4)	2.121 (3)
Tc–N2F	2.127 (4)	2.131 (3)
Tc–N2B	2.059 (4)	2.125 (4)
Tc–N3F	2.062 (3)	2.083 (4)
Tc–N3B	2.063 (4)	2.088 (3)
N1F–C12	1.300 (7)	1.298 (5)
C12–C13	1.454 (7)	1.448 (7)
C13–N1B	1.310 (7)	1.296 (5)
C12–C11	1.487 (9)	1.491 (7)
C13–C14	1.492 (7)	1.500 (7)
N1B–O1B	1.357 (5)	1.382 (5)
N2B–O2B	1.371 (5)	1.373 (5)
N3B–O3B	1.373 (5)	1.352 (5)
O1F–O2F	3.837 (6)	3.342 (5)
O1F–O3F	2.494 (6)	2.515 (4)
O2F–O3F	2.559 (4)	2.512 (5)
O1B–O2B	2.506 (5)	3.402 (4)
O1B–O3B	2.440 (5)	2.518 (4)
O2B–O3B	2.448 (4)	2.525 (5)
O1F–H1F	1.1	1.1
O3F–H1F	1.5	1.5
O2F–H2F	1.1	1.1
O3F–H2F	1.6	1.6
O1B–H1B		1.2
O3B–O1B		1.4
O2B–H2B		1.0
O3B–H2B		1.6
O1B–B	1.528 (8)	
O2B–B	1.500 (6)	
O3B–B	1.480 (5)	
C41–B	1.585 (8)	

as an intermediate in this reaction. It appears from these results that the formation of the BATO complexes via SnCl₂ reduction of ^{99}TcO₄⁻ may proceed via the sequence

$$\text{TcO}_4^- + 3\,\text{oxime} + 2\text{SnCl}_2 \rightarrow \text{Tc(oxime)}_3(\mu\text{-OH})\text{SnCl}_3$$

$$\text{Tc(oxime)}_3(\mu\text{-OH})\text{SnCl}_3 \rightleftharpoons [\text{TcCl(oxime)}_3] \xrightarrow[\text{(OH)}_2\text{BR}]{} \text{TcCl(oxime)}_3\text{BR}$$

Structure of TcCl(DMG)₃MeB. This complex (Figure 4) is similar to other BATO complexes that we have crystallographically characterized[1,3a] but is more precisely defined. The technetium is seven-coordinate; three N-bonded dioxime ligands and a covalently bonded chlorine atom in a face-capped trigonal prismatic array make up the donor set. A tetrahedral boron caps the three dioxime oxygen atoms on one side of the molecule. The remaining three oxime oxygens form an isosceles triangle defined by O1F–O2F–O3F. These atoms are joined by two strong intramolecular hydrogen bonds (O1F⋯O3F = 2.494 (6) Å, O2F⋯O3F = 2.559 (4) Å). The two bridging protons, one apparently bonded to O1F and the other to O2F (e.g. O1F–H1 = 1.1 Å, H1–O3F = 1.5 Å), were clearly evident on difference maps of TcCl(DMG)₃MeB.

Structure of TcCl(DMG)₃. The X-ray crystal structure determination of this seven-coordinate complex reveals that the donor set and ligand geometry about Tc are similar to that seen in the BATO complexes. Selected bond distances and bond angles in TcCl(DMG)₃MeB and TcCl(DMG)₃ are compared in Tables III and IV. An ORTEP diagram of the C_{2v} symmetric structure of TcCl(DMG)₃ is shown in Figure 5. As in the BATO structure, there are two equivalent dioxime ligands and one unique dioxime, which lie in a "paddle wheel" array about the Tc. The Tc–N bond distances for the two equivalent DMG ligands in TcCl(DMG)₃ range from 2.120 (4) to 2.131 (3) Å. The Tc–N bond distances of the unique DMG are shorter, at 2.086 (4) Å. The latter bond distances are similar to the average Tc–N distances found in Tc(DMG)₃(μ-OH)SnCl₃ (2.089 Å)[5a] and in the Tc(V)–oxo amine–oxime complexes (2.08 Å)[12] reported previously.

Table IV. Selected Bond Angles (deg) for TcCl(DMG)₃MeB and TcCl(DMG)₃

	TcCl(DMG)₃MeB	TcCl(DMG)₃
N1F–Tc–N1B	72.9 (2)	71.2 (2)
N2F–Tc–N2B	72.6 (2)	71.1 (1)
N3F–Tc–N3B	71.6 (2)	71.0 (2)
N1B–Tc–Cl	84.7 (1)	79.9 (1)
N1F–Tc–Cl	79.1 (1)	80.9 (1)
N2B–Tc–Cl	83.0 (1)	81.5 (1)
N2F–Tc–Cl	80.6 (1)	80.5 (1)
N3B–Tc–Cl	152.56 (9)	144.3 (1)
N3F–Tc–Cl	135.9 (1)	144.7 (1)
N1F–C12–C13	113.5 (5)	112.4 (4)
C12–C13–N1B	112.6 (4)	113.9 (4)
N1F–Tc–N3F	76.2 (2)	78.4 (2)
N1B–Tc–N3B	77.6 (2)	77.9 (1)
N1B–O1B–B	114.8 (3)	
N2B–O2B–B	113.7 (3)	
N3B–O3B–B	115.3 (4)	
O1B–B–C41	107.3 (4)	
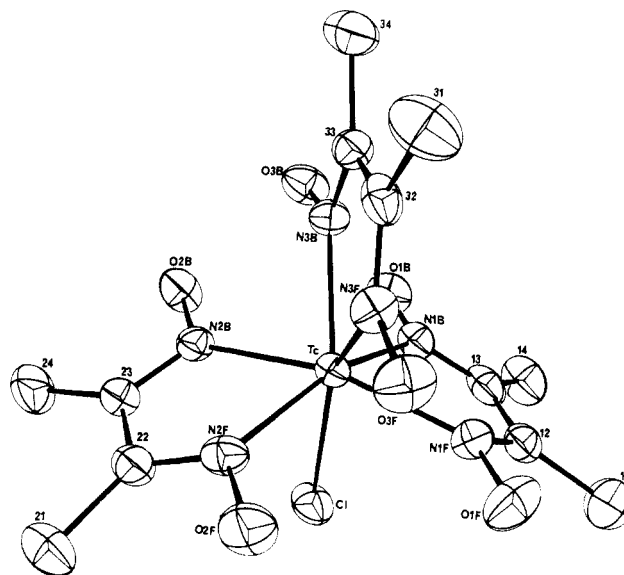
Figure 5. ORTEP diagram of TcCl(DMG)₃.

For TcCl(DMG)₃, both electron density in the difference maps and close intramolecular O⋯O contacts (average = 2.518 (5) Å) between O1F–O3F, O2F–O3F, O1B–O3B, and O2B–O3B clearly indicate the presence of four bridging hydrogen bonds between these atoms. As in the structure of TcCl(DMG)₃MeB, the proton bridges appear to be asymmetric (Table III). As the complex is neutral, the oxidation state of TcCl(DMG)₃ can be assigned as Tc(III).

In both TcCl(DMG)₃ and TcCl(DMG)₃MeB, the seventh position on Tc is occupied by a chloride ligand, which is trans to the unique oxime. The Tc–Cl distance in both complexes (2.415 (1) and 2.411 (1) Å, respectively) is slightly longer than that found in the six-coordinate complexes *trans*-[TcCl₂(diars)₂]Cl (2.33 Å)[13] and (NH₄)₂TcCl₆ (2.35 Å)[14] and shorter than that found in the eight-coordinate complex [TcCl₄(diars)₂]PF₆ (2.44 Å).[15] X-ray photoelectron spectroscopy[16] has shown the binding energy of the chloride in the BATO complexes to be intermediate to that of a covalently and ionically bonded chloride. We have found this chloride ligand to be moderately labile; it can be easily replaced

(12) Jurisson, S.; Schlemper, E. O.; Troutner, D. E.; Canning, L. R.; Nowotnik, D. P.; Neirinckx, R. D. *Inorg. Chem.* **1986**, *25*, 543.
(13) Elder, R. C.; Whittle, R.; Glavan, K. A.; Johnson, J. F.; Deutsch, E. *Acta Crystallogr., Sect. B* **1980**, *36*, 1662.
(14) Elder, R. C.; Estes, G. W.; Deutsch, E. *Acta Crystallogr., Sect. B* **1979**, *35*, 136.
(15) Glavan, K. A.; Whittle, R.; Johnson, J. F.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1980**, *102*, 2103.
(16) Thompson, M.; Nunn, A. D.; Treher, E. N. *Anal. Chem.* **1986**, *58*, 3100.

by other halogens,[1] or by OH⁻.[17]

Some of the inter-oxygen distances differ markedly in the $TcCl(DMG)_3MeB$ and $TcCl(DMG)_3$ structures. In the BATO complex, the boron cap draws together the three oxime oxygens involved in this cap and forces the three oxime oxygens on the other side of the molecule (O1F, O2F, O3F) to spread apart. The distance O1F–O2F, on the uncapped side of the molecule is 3.837 (6) Å; considerably longer than the corresponding distance O1B–O2B (2.506 (5) Å) on the capped end of the complex. This asymmetry is clearly due to the constraints of the boron cap because in the uncapped complex $TcCl(DMG)_3$ the corresponding O⋯O distances are similar on both ends of the molecule (O1F–O2F = 3.342 (5), O1B–O2B = 3.402 (4) Å).

It is of interest to note that previously reported uncapped tris(dioxime) complexes (which are all six-coordinate) exhibit more or less distorted octahedral geometry[18] and adopt a trigonal geometry only after capping. By contrast, both the seven-coordinate uncapped tris(dioxime) complex $TcCl(DMG)_3$ and the corresponding monocapped BATO complex have trigonal coordination geometry. In fact, the dihedral angle (129°) between the planes of the two equivalent dioxime ligands in $TcCl(DMG)_3$ more closely approaches the idealized trigonal prismatic value (120°) than does the corresponding angle (144°) in the BATO compound.

The seven-coordination of the complexes reported here is unusual for technetium (six-coordinate complexes are far more common[19]) but is not unique.[19,20] As yet, there are no distinct trends that would allow the prediction of six- or seven-coordination in technetium, except that almost all seven-coordinate Tc complexes that have been characterized to date (regardless of donor set) are compounds of technetium(III).[19,20] One apparent exception to this trend is the seven-coordinate complex $Tc(DMG)_3(\mu\text{-}OH)SnCl_3$, which was tentatively assigned[5] as Tc(V). As we have found that this complex can be smoothly converted to the Tc(III) compounds $TcCl(DMG)_3$ and $TcCl(DMG)_3BR$ in the absence of reductant, we reinvestigated the oxidation state of this tin-capped complex.

Oxidation State of $Tc(oxime)_3(\mu\text{-}OH)SnCl_3$. The crystal structure analysis[5] of $Tc(DMG)_3(\mu\text{-}OH)SnCl_3$ did not reveal the degree of protonation of the four (non-tin-bonded) oxime oxygens or of the bridging oxygen atom. Therefore, the formal oxidation states of the Sn and Tc in this complex could not be assigned with certainty. On the basis of the Sn–Cl bond lengths (2.36–2.41 Å) and the six-coordination about tin, Deutsch et al. assigned the Sn as Sn(IV), an assignment that we believe is correct. The complex is diamagnetic;[7] therefore, it must contain Tc in the oxidation state I, III, V, or VII. Only Tc(III) and Tc(V) are chemically feasible. If the complex is Tc(V), two protons are required to give the complex the neutral charge observed by conductivity measurements. If the complex is Tc(III), four protons are required for charge balance.

ligand	charge	
	Tc(III)	Tc(V)
3 DMG (deprotonated)	–6	–6
bridging oxo	–2	–2
SnCl₃	+1	+1
Tc	+3	+5
protons required for charge balance	+4	+2
mol wt	686.35	684.35

(17) (a) Hirth, W.; Jurisson, S.; Linder, K.; Feld, T.; Nunn, A. D. *J. Nucl. Med.* **1988**, *29*, 5, 800. (b) Hirth, W. H.; Jurisson, S.; Linder, K.; Feld, T.; Nunn, A. D. *J. Labelled Compd. Radiopharm.* **1989**, *26*, 48.
(18) (a) Simonov, Y. A.; Botoshanskii, M. M.; et al. *Koord. Khim.* **1981**, *7*, 612. (b) Lenstra, A. T. H.; Van Loock, J.; Tyrlik, S. K. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1983**, *31*, 23. (c) Endres, H. *Acta Crystallogr., Sect. C* **1985**, *41*, 1423.
(19) Melnik, M.; Van Lier, J. E. *Coord. Chem. Rev.* **1987**, *77*, 275.
(20) See, for example: (a) Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1978**, *5*, 373. (b) Baldas, J.; Bonnyman, J.; Mackay, M. F.; Williams, G. A. *Aust. J. Chem.* **1984**, *37*, 751. (c) Mazzi, U.; Bismondo, A.; Kotsev, N.; Clemente, D. A. *J. Organomet. Chem.* **1977**, *135*, 177.
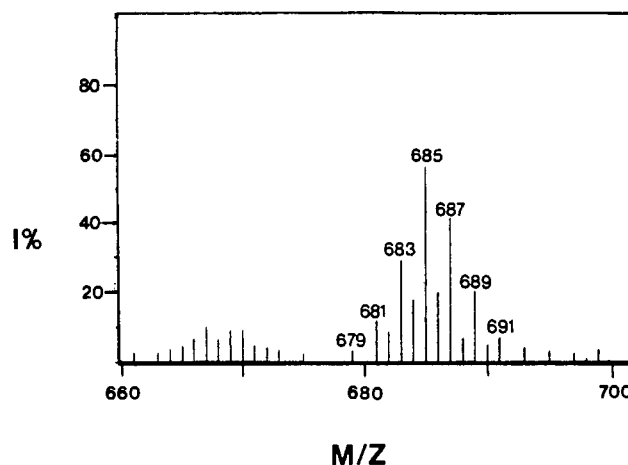
M/Z

Figure 6. Fast-atom-bombardment mass spectrum (negative mode) of the molecular ion cluster of $Tc(DMG)_3(\mu\text{-}OH)SnCl_3$ (glycerol matrix).

Table V. Relative Abundance of the Peaks in the Protonated Molecule (M − H)⁻ of $Tc^{III}(DMG)_3(\mu\text{-}OH)SnCl_3$ under FAB (Negative Mode) Conditions for Observed vs Calculated Spectra

	rel abundance	
m/z	obsd	calcd
679	5.2	2.5
680	0.86	0.9
681	20.7	23.6
682	15.0	16.0
683	51.7	61.6
684	31.5	34.8
685	100.0	100.0
686	35.3	32.9
687	72.4	75.1
688	12.0	16.7
689	36.2	36.6
690	8.6	6.3
691	12.0	14.1
692	0.0	2.2
693	8.6	3.5

We have examined the positive and negative FAB spectra of both the DMG and CDO tin-capped complexes to distinguish between these two possibilities. To our knowledge, these are the first tin–technetium binuclear complexes to be studied by mass spectrometry. (Costello et al.[21] have reported the presence of both Tc and Sn imidodiacetate complexes in a radiopharmaceutical kit, but binuclear Tc–Sn species were not observed.)

Under positive and negative FAB conditions, both the CDO and DMG complexes gave peaks at a mass which indicates that they are Tc(III) compounds. Since Sn has 10 isotopes and there are three Cl atoms (Cl 35/37) on either molecule, a complex molecular cluster is expected. For the complex $Tc^{III}(DMG)_3(\mu\text{-}OH)SnCl_3$, the most intense peak of the (M–H)⁻ cluster should fall at m/z 685, as is observed in Figure 6. If the complex were Tc(V), this cluster would peak at m/z 683. The observed and calculated isotope patterns for $Tc^{III}(DMG)_3(\mu\text{-}OH)SnCl_3$ match very well, and no significant contribution from an ion corresponding to a Tc(V) assignment is seen (Table V). Under positive FAB conditions, the largest peak of the (M + H)⁺ cluster falls at m/z 687; again consistent with a Tc(III) assignment. Several lower mass ion clusters are also seen in the FAB⁺ spectrum of $Tc(DMG)_3(\mu\text{-}OH)SnCl_3$. Most of these can be assigned as compounds where the SnCl₃ group has lost Cl⁻ (as HCl) or substituted OH⁻ for Cl⁻. In addition, the SnCl₃ cap is lost to give $Tc(DMG)_3^+$. The positive FAB spectrum of $Tc(CDO)_3(\mu\text{-}OH)SnCl_3$ is consistent with that of the DMG analogue described above; the (M + H)⁺ ion cluster, which peaks at m/z 765, and

(21) Costello, C. E.; Brodack, J. W.; Jones, A. G.; Davison, A.; Johnson, D. L.; Kasina, S.; Fritzberg, A. *J. Nucl. Med.* **1983**, *24*, 353.

$(M - H)^-$ at m/z 763 both indicate a Tc(III) assignment.

It should be noted that the Tc(III) ions in the spectra of these complexes could be due to facile reduction of Tc(V) complexes in the FAB matrix, a phenomenon that several authors have noted for compounds that are easily reduced.[22] For compounds that undergo such beam-induced redox chemistry, changing the FAB matrix will often change the ions observed.[22e] We have found that changing the FAB matrix from glycerol to thioglycerol (which is relatively reducing[22c,e]) or to 3-nitrobenzyl alcohol (which is oxidizing[22e,23]) caused *no change* in the FAB spectrum of these tin-capped compounds. A molecular ion that suggests a Tc(III) formulation was seen in all cases. Thus, we believe that no change in oxidation state occurred during the mass spectral analysis.

The presence of four exchangeable protons was confirmed by running the spectrum of deuterated $Tc(DMG)_3(\mu\text{-OD})SnCl_3$ from thioglycerol-d_3 and from glycerol-d_3 under both positive and negative FAB conditions. On deuteration, the cluster in positive FAB should move 5 amu $(MH_4 + H)^+ \rightarrow (MD_4 + D)^+$, and under negative FAB conditions, the cluster should move 3 amu $(MH_4 -H)^- \rightarrow (MD_4 - D)^-$. The expected shifts were seen in both cases.

Chemical evidence also suggests that the $Tc(oxime)_3(\mu\text{-OH})$-$SnCl_3$ complexes are Tc(III). Treatment of the Tc(III) TcCl-$(oxime)_3$ complexes (oxime = DMG, CDO) with $SnCl_4$ causes quantitative formation of $Tc(oxime)_3(\mu\text{-OH})SnCl_3$ (eq 4). The facile high-yield conversion of these tin-capped complexes to the Tc(III) BATO complexes via treatment with a boronic acid and to the Tc(III) $TcCl(oxime)_3$ complexes in the absence of reducing agents also suggests a Tc(III) assignment.

Location of the Protons. The mass spectra of these tin-capped complexes suggests that they contain four exchangeable protons but cannot indicate the position of these protons. However, in the ^1H NMR spectrum of $Tc(DMG)_3(\mu\text{-OH})SnCl_3$, a broad peak is seen at 18.6 ppm (1 H), a chemical shift that is characteristic of bridging protons that are shared by two oxime oxygen atoms.[9] This proton we assign to the position where the closest O–O contact (2.36 Å) is seen in the crystal structure of the complex (Figure 2). Another broad peak falls at 6.2 ppm (0.8 H); this we tentatively assign to a position on the Tc–OH–Sn bridge. The remaining two protons appear to exchange with the waters of hydration of this complex (3 H₂O) and contribute to the water peak centered at 2.3 ppm (8 H). These two protons are tentatively assigned to the two non-hydrogen-bonded oxygens on the unique (antiparallel) dioxime ligand. All of these protons undergo facile exchange when the sample is treated with D_2O.

Conclusion

The formation of the BATO complexes $TcCl(oxime)_3BR$ from $^{99}TcO_4^-$, when $SnCl_2$ is used as the reductant, proceeds through two Tc(III) intermediates, $Tc(oxime)_3(\mu\text{-OH})SnCl_3$ and $TcCl(oxime)_3$. This indicates clearly that vicinal dioximes such as DMG or CDO can stabilize the oxidation state Tc(III). Formation of the tin-capped complexes from TcO_4^- is quite rapid, indicating that, as suggested by Deutsch,[5a] the tin–hydroxy bridge in this complex may form via a $Sn^{II}Cl_3$—O=Tc species. In acid solution, the tin cap of $Tc(oxime)_3(\mu\text{-OH})SnCl_3$ is lost, and $TcCl(oxime)_3$ is formed. During this step, the unique oxime in the tin-capped species, which is antiparallel to the other two dioximes, must rearrange to the structure seen in the BATO and $TcCl(oxime)_3$ complexes. Once the tin cap is lost and the third dioxime has rearranged, the uncapped intermediate is properly oriented for capping by the boronic acid. Capping to form the BATO complexes $TcCl(oxime)_3BR$ from $TcCl(oxime)_3$ then proceeds rapidly and in high yield.

(22) (a) Cooper, R.; Unger, S. *J. Antibiot.* **1985**, *38*, 24. (b) Pelzer, G.; De Pauw, E.; Dung, D. V.; Marien, J. *J. Phys. Chem.* **1984**, *88*, 5065. (c) De Pauw, E. *Mass Spectrom. Rev.* **1986**, *5*, 191. (d) Williams, D. H.; Findeis, A. F.; Naylor, S.; Gibson, B. W. *J. Am. Chem. Soc.* **1987**, *109*, 1980. (e) Costello, C. In *Mass Spectrometry in Biomedical Research*; Gaskell, S. J., Ed.; Wiley & Sons: New York, 1986; p 31.

(23) (a) Meili, J.; Seibl, J. *Org. Mass Spectrom.* **1984**, *19*, 581. (b) Vetter, W.; Meister, W. *Org. Mass Spectrom.* **1985**, *20*, 267.