Inorg. Chem. **1989**, *28*, 3411–3416

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Monocapped Tris(dioxime) Complexes of Technetium(III): Synthesis and Structural Characterization of $TcX(dioxime)_3B$–R (X = Cl, Br; dioxime = Dimethylglyoxime, Cyclohexanedione Dioxime; R = CH_3, C_4H_9)

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Received December 21, 1988

Monocapped boronic acid adducts of technetium tris(dioxime) complexes (BATO), $TcX(dioximeH)_2(dioxime)B$–R, where X = Cl or Br, dioxime = cyclohexanedione dioxime or dimethylglyoxime, and R = methyl or butyl, have been prepared by template synthesis starting with pertechnetate and stannous ion, $(N(C_4H_9)_4)[TcOCl_4]$, or $M_2[TcX_6]$ (M = NH_4, K; X = Cl, Br). These seven-coordinate Tc(III) compounds are the first examples of tris(dioxime) complexes in which one and only one oxygen of each of the three dioximes is joined to a common cap atom (boron). The crystal structures of three of the BATO complexes have been determined. $TcBr(CDO)_3BCH_3$ (**1**): $a = b = 11.056$ (6) Å, $c = 17.321$ (9) Å, trigonal space group $P3_1$, $Z = 3$, $R = 0.06$. $TcBr(DMG)_3BC_4H_9$ (**3**): $a = 13.143$ (2) Å, $b = 18.077$ (3) Å, $c = 19.858$ (2) Å, $\beta = 100.76$ (1)°, monoclinic space group $P2_1/c$, $Z = 8$, $R = 0.05$. $TcBr(CDO)_3BC_4H_9$ (**5**): $a = 25.357$ (7) Å, $b = 13.423$ (4) Å, $c = 19.637$ (5) Å, $\beta = 124.97$ (2)°, monoclinic space group $C2/c$, $Z = 8$, $R = 0.06$. The three dioxime oxygens on the uncapped end of the molecule are *intra*molecularly hydrogen bonded to two bridging protons. A halogen occupies the seventh coordination site.

Introduction

Clathrochelates, metal complexes in which the metal atom is both coordinated and surrounded by a cage of ligand atoms, were first proposed by Busch.[2] One approach to the preparation of clathrochelates involves a template reaction between a transition metal containing three bidentate donors and a reagent selected to join or cap all three bidentate ligands at each end of the complex. Examples of such clathrochelates are metal tris(dioxime) bis(boron-capped) complexes, $M(dioxime)_3(B\text{–}R)_2$ (M = Co, Fe, Ru), which have been known for a number of years.[3–8] The corresponding monocapped compounds, however, have never been reported. We describe here the synthesis and characterization of a unique family of seven-coordinate monocapped boronic acid adducts of technetium tris(dioxime) (BATO) complexes. The complexes discussed here are shown in Figure 1. They will be identified by number or by the trivial name TcX $(dioxime)_3B$–R, where X = Cl or Br, dioxime = cyclohexanedione dioxime or dimethylglyoxime, and R = CH_3 or n-C_4H_9.[9]

The increasing interest in the coordination chemistry of technetium, studied with ^{99}Tc, is due primarily to the importance of ^{99m}Tc containing radiopharmaceuticals in diagnostic nuclear medicine procedures. The technetium(III) compounds reported here are easily prepared at both the ^{99}Tc (millimolar) and ^{99m}Tc (nanomolar) levels. Two ^{99m}Tc BATO complexes are undergoing clinical evaluation as agents for imaging myocardial and cerebral perfusion.[10–12]

Experimental Section

Materials. Technetium, as solid $NH_4{}^{99}TcO_4$, was purchased from Oak Ridge National Laboratory and recrystallized from water. $(N(Bu)_4)[TcOCl_4]$, $(NH_4)_2[TcCl_6]$, $(NH_4)_2[TcBr_6]$, and $K_2[TcBr_6]$ were prepared from NH_4TcO_4 by using published procedures.[13,14] Cyclohexanedione dioxime (CDO), dimethylglyoxime (DMG), and 1-butaneboronic acid were purchased from Aldrich. Methylboronic acid was obtained from Alfa Products. All solvents were used as received; distilled, deionized water was used throughout.

Apparatus. ^{1}H NMR data were recorded in $CDCl_3$ at 30 °C on a 400-MHz JEOL-GX-400 spectrometer with TMS as the internal standard. Infrared spectra were obtained from KBr pellets on a Sirius 100 spectrophotometer in the range 4000–500 cm^{-1}. Conductivity measurements (10^{-3} M solutions in acetonitrile) were made by using a YSI Model 32 conductance meter. Elemental and mass spectral analyses were performed by the Analytical R&D Department, The Squibb Institute for Medical Research, Princeton, NJ. Fast atom bombardment (FAB) mass spectra of samples dissolved in a thioglycerol or dithiothreitol–dithioerythritol matrix were recorded with a VG-ZAB-2F mass spectrometer.[15]

Synthesis. The methods outlined below in representative examples were used in the preparation of the BATO complexes. The method of synthesis and elemental analysis data for **1**–**6** are presented in Table I. The reactions were run in flasks open to the atmosphere. Products were dried at room temperature for at least 12 h at 1 Torr over Drierite.

Method 1. From $K_2[TcBr_6]$. Preparation of $TcBr(CDO)_3BCH_3$ (1). A solution of $K_2[TcBr_6]$ (160 mg, 0.242 mmol) in 3 mL of 5% HBr, prepared by dissolution at room temperature, was added to a solution containing CDO (436 mg, 3.1 mmol) and methylboronic acid (260 mg, 4.3 mmol) dissolved in 15 mL of ethanol. The resulting orange-red solution was heated with stirring at ca 50 °C for 3 h. During this time a bright orange precipitate formed. This solid was isolated by filtration, washed with 5 mL of 5% HBr and 10 mL of water, and dried in vacuo overnight. The solid was recrystallized by dissolving in 15 mL of boiling ethanol, adding 0.25 mL of 5% HBr, and cooling slowly. The red crystals that formed after 30 min were collected by filtration and washed twice with 1.5 mL of ethanol. Yield: 85 mg, 56% based on Tc.

Method 2. From $(NH_4)[TcO_4]$. Preparation of $TcCl(DMG)_3BC_4H_9$ (4). DMG (116 mg, 1.0 mmol), 1-butaneboronic acid (34 mg, 0.33 mmol), NaCl (150 mg, 2.57 mmol), and $(NH_4)[TcO_4]$ (30 mg, 0.17 mmol) were dissolved in warm ethanol (30 mL) and 1 M HCl (10 mL). $SnCl_2$ (151 mg, 0.80 mmol in 1 mL of 6 M HCl) was added dropwise, giving an immediate red solution. The reaction was stirred for 1.5 h. Then, 3 M HCl (5 mL) was added to give an orange precipitate. The solid was filtered and washed with 2 mL of H_2O. The solid was recrystallized by dissolving in 10 mL of boiling ethanol and cooling slowly to room temperature. Yield: 25 mg, 0.044 mmol, 26% based on Tc.

Method 3. From $[N(C_4H_9)_4][TcOCl_4]$. Preparation of $TcCl(CDO)_3BC_4H_9$ (6). A slurry of $[N(C_4H_9)_4][TcOCl_4]$ (130 mg, 0.26 mmol) in 5 mL of ethanol was added to a solution of CDO (480 mg, 3.38 mmol) and 1-butaneboronic acid (700 mg, 6.87 mmol) in 10 mL of ethanol. The resulting solution immediately turned red orange in color. The solution

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Table I. Compounds, Preparation Method, and Analyses

			elem anal., wt %						
			calcd			obsd			
compd	prep method	% yield	C	H	N	C	H	N	conductivity, $cm^2\ mol^{-1}\ \Omega^{-1}$
1	1	56	36.38	4.66	13.40	36.42	4.56	13.12	1.4
2	2	26	39.16	5.02	14.42	39.41	5.05	14.31	2.3
3	1	20	32.51	4.94	14.22	32.51	5.07	14.12	2.1
4	2	26	35.15	5.35	15.38	35.31	5.58	14.97	1.3
5	1	39	39.48	5.27	12.56	39.58	5.50	12.43	0.91
6	3	43	42.29	5.65	13.45	42.16	5.54	13.21	0.78

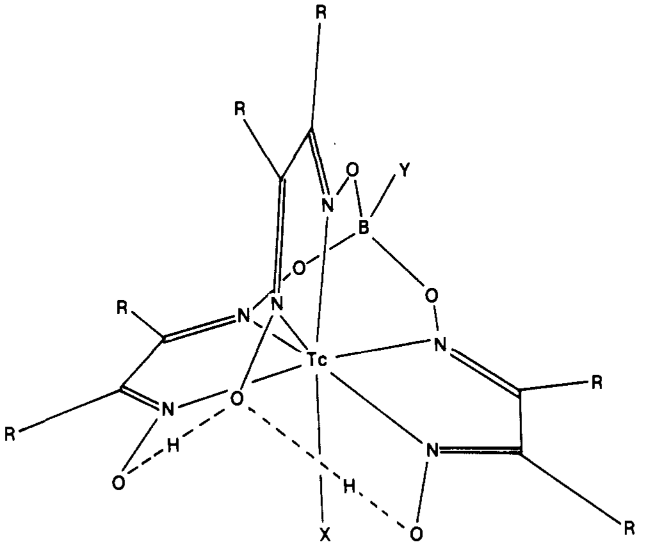

Figure 1. General structure of the BATO complexes, TcX(dioxime)$_3$B–Y.

structure	X	Y	R
1	Br	CH_3	$-CH_2CH_2-$
2	Cl	CH_3	$-CH_2CH_2-$
3	Br	*n*-Bu	CH_3
4	Cl	*n*-Bu	CH_3
5	Br	*n*-Bu	$-CH_2CH_2-$
6	Cl	*n*-Bu	$-CH_2CH_2-$

was stirred at room temperature for 24 h. HCl (1 M, 15 mL) was added to the reaction solution to precipitate an orange solid. The suspension was heated to a boil until all the solid dissolved, and the solution was concentrated to ca 20 mL. As the solution cooled, deep red crystals precipitated. The product was washed with 5 mL of 1 M HCl and 5 mL of water and dried in vacuo at room temperature. The solid was recrystallized from 8 mL of acetonitrile by dropwise addition of HCl (3 mL, 1 M). Yield: 69 mg, 43% based on Tc.

X-ray Analysis. Crystal data and some details of the structure refinements for compounds **1**, **3**, and **5** are given in Table II. Weissenberg and precession films were used to confirm the space group assignments. 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 on a Syntex $P2_1$ diffractometer at 23 °C with the θ–2θ variable scan technique and were corrected for Lorentz polarization factors and for absorption by the DIFABS[16] procedure. Background counts were collected at the extremes of the scan for half 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 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.[17] 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 $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

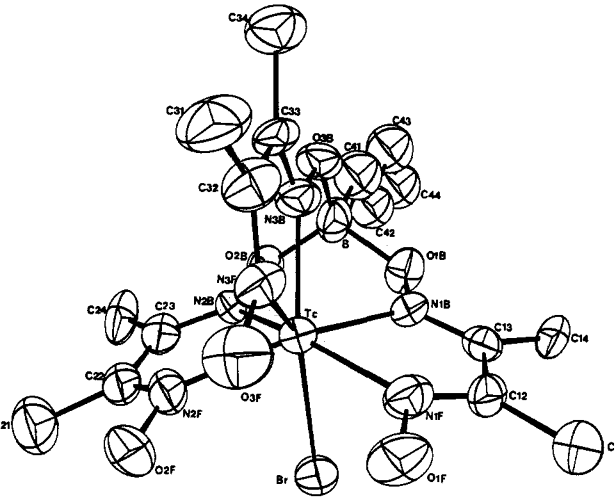

Figure 2. Perspective ORTEP drawing of one of the molecules in the asymmetric unit of **3**. All non-hydrogen atoms are represented by 50% probability ellipsoids having the slope, orientation, and relative position consistent with refined anisotropic thermal parameters. Hydrogen atoms have been omitted.

All three crystal structures contain some molecular disorder, which has limited the accuracy of the determinations. Structures **3** and **5** and all other butyl derivatives that we have examined crystallographically have been found to have site-disordered butyl groups. Two orientations (3:1) of the butyl chains were observed for **5**. The asymmetric unit of **3** contains two independent complexes that differ significantly only in the conformation of the butyl side chain. One of the molecules has site disorder of one atom of the butyl chain (C43′ and C43A′ (3:1)). Probable disorder in the other molecule, as evidenced by the large apparent temperature factors in the butyl chain, could not be resolved. In addition, complexes **1** and **5** show conformational disorder of the cyclohexyl rings: the positions of the outwardmost methylene carbon atoms are poorly defined with unreasonably large apparent temperature factors, probably due to the presence of two types of half-chair conformations. Consequently, most of the hydrogen atoms are also disordered. In no case were reliable hydrogen positions evident in difference maps.

The coordinates of all non-hydrogen atoms (except the site-disordered minor component atoms C43A′ of **3** and C42′–C44′ of **5**) were refined as well as anisotropic temperature factors for all ordered atoms of **3** and **5** and the Tc and Br atoms of **1**. Temperature factors for the other ordered atoms of **1** were refined isotropically. All disordered atoms were assigned fixed isotropic temperature factors.

Atomic coordinates are given in Tables III–V. An ORTEP[18] drawing of one of the molecules in the asymmetric unit of **3**, which is representative of all of the BATO complexes, is shown in Figure 2.

Results and Discussion

Synthesis. The BATO complexes **1**–**6** were prepared by stannous reduction of pertechnetate in the presence of the ligands or from $[TcOCl_4]^-$ or $[TcX_6]^{2-}$ (X = Cl, Br). Reactions of

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Table II. Crystallographic Data

	1	**3**	**5**
a, Å	11.056 (6)	13.143 (2)	25.357 (7)
b, Å	11.056 (6)	18.077 (3)	13.423 (4)
c, Å	17.321 (9)	19.858 (2)	19.637 (5)
α, deg	90.00	90.00	90.00
β, deg	90.00	100.76 (1)	124.97 (2)
γ, deg	120.00	90.00	90.00
V, Å^3	1834 (2)	4635 (2)	5477 (6)
space group	$P3_1$	$P2_1c$	$C2/c$
D_{obs}, g cm^{-3}	1.69	1.70	1.62
D_{calc}, g cm^{-3}	1.7	1.69	1.62
formula	$TcBrO_6N_6C_{19}BH_{29}$	$TcBrO_6N_6C_{16}BH_{29}$	$TcBrO_6N_6C_{22}BH_{35}$
fw	627.19	591.15	669.27
Z	3	8	8
color	orange red	red	red
dimens, mm	0.1 × 0.05 × 0.03	0.33 × 0.35 × 0.45	0.35 × 0.15 × 0.1
μ, cm^{-1}	71.9	23.6	20.0
transm factors		0.78–1.26	0.9–1.10
measd reflcns	$h,\pm k,l$	$h,k,\pm l$	$h,k,\pm l$
2θ max, deg	115	55	50
scan rate, deg/min	2–29.3	10–29.3	10–29.3
λ source, Å	1.5418	0.71069	0.71069
monochromator	graphite	graphite	graphite
N_{ref}[a]	2762	10107	9407
N_{uni}[b]	1736	9648	4908
N_{obs}[c]	993	3554	1832
N_{var}[d]	140	514	280
ERRWT[e]	1.41	1.38	1.81
SHIF/ERR[f]	0.02	0.06	0.00
R	0.063	0.053	0.060
R_w	0.065	0.055	0.067

[a] Total number of measured reflections within 2θ max. [b] Total number of symmetry-independent measured reflections. [c] Total number of "observed" reflections with $I \geq 3\sigma(I)$ used for refinements. [d] Number of variables in least-squares refinements. [e] Error in an observation of unit weight. [f] Maximum shift/error during final cycle of refinement.

$TcOCl_4^-$ to give $Tc^V{=}O$ complexes by ligand substitution are well-known.[19,20] Much less common is the reaction where the Tc=O bond in $TcOCl_4^-$ is displaced, as occurs in the reactions described here and also in the reported[21] synthesis of $Tc(mdtc)_4$ (mdtc = morpholine-*N*-carbodithioate) from $[TcOCl_4]^-$.

The preparation of these compounds by Sn(II) reduction of pertechnetate is illustrated in the following equation:

$$TcO_4^- + 3CDOH_2 + CH_3B(OH)_2 + 2SnCl_3^- + 6H^+ \rightarrow TcCl(CDOH)_2(CDO)(BCH_3) + 6H_2O + 5Cl^- + 2Sn(IV)$$

In some cases using TcO_4^-, less than 2 equiv of tin(II) were used without a reduction in yield. This suggests that reduction by the ethanol/HCl reaction medium and/or ligand(s) must also take place, as in the reactions with TcX_6^{2-} and $TcOCl_4^-$.

Even in reactions where a large (2–10-fold) excess of boronic acid was used, only the monocapped species was isolated and in a yield similar to that observed when stoichiometric amounts of the reagents were used.[22]

Characterization. Conductance measurements (10^{-3} M in acetonitrile) indicate that the complexes are neutral. The measured values, given in Table I, range from 0.78 to 2.1 Ω^{-1} cm^2 mol^{-1}, well below the reported range for a 1:1 electrolyte in acetonitrile.[23] The infrared spectra show several dominant bands also seen in the reported biscapped dioxime boronic acid transition-metal complexes.[4,7] The assignments are as follows: 1550–1575 (C=N stretch), 1232–1233 and 1058–1060 cm^{-1} (N—O stretch), 1203–1207 and 806–811 (B—O stretch), and 3437–3441 cm^{-1} (O—H stretch).

Table III. Positional Parameters and Their Estimated Standard Deviations for Structure **1**

atom	*x*	*y*	*z*
Tc	0.0590 (2)	0.2070 (2)	0.000
Br	0.0961 (3)	0.1196 (3)	−0.1292 (2)
N1F	−0.124 (2)	0.004 (2)	−0.004 (1)
N2F	0.062 (2)	0.359 (2)	−0.078 (1)
N3F	−0.090 (2)	0.246 (2)	0.046 (1)
N1B	0.111 (2)	0.064 (2)	0.045 (1)
N2B	0.261 (2)	0.358 (2)	−0.014 (1)
N3B	0.114 (2)	0.282 (2)	0.109 (1)
O1F	−0.250 (2)	−0.019 (2)	−0.038 (1)
O2F	−0.054 (2)	0.350 (2)	−0.109 (1)
O3F	−0.203 (2)	0.219 (2)	0.003 (1)
O1B	0.239 (1)	0.104 (1)	0.0758 (9)
O2B	0.369 (1)	0.351 (1)	0.023 (1)
O3B	0.237 (1)	0.301 (1)	0.1453 (9)
C11	−0.230 (3)	−0.252 (3)	−0.008 (2)
C12	−0.111 (2)	−0.102 (2)	0.012 (1)
C13	0.026 (2)	−0.068 (2)	0.043 (2)
C14	0.053 (2)	−0.175 (2)	0.071 (1)
C15	−0.055 (2)	−0.325 (2)	0.029 (1)
C16	−0.190 (2)	−0.357 (2)	0.031 (2)
C21	0.205 (3)	0.548 (3)	−0.175 (2)
C22	0.176 (2)	0.442 (2)	−0.108 (2)
C23	0.298 (2)	0.444 (3)	−0.068 (2)
C24	0.450 (3)	0.538 (3)	−0.101 (2)
C25	0.446 (2)	0.620 (2)	−0.172 (2)
C26	0.350 (2)	0.630 (2)	−0.202 (2)
C31	−0.197 (2)	0.309 (2)	0.152 (2)
C32	−0.084 (2)	0.293 (2)	0.114 (2)
C33	0.040 (2)	0.314 (2)	0.154 (1)
C34	0.073 (2)	0.363 (2)	0.236 (1)
C35	−0.025 (2)	0.422 (2)	0.262 (2)
C36	−0.170 (2)	0.331 (2)	0.241 (2)
B	0.323 (2)	0.262 (2)	0.094 (2)
C41	0.466 (2)	0.290 (2)	0.135 (2)

Proton NMR spectral assignments for two representative complexes are given in Table VI. One of the dioxime groups is distinguishable from the other two equivalent dioximes. Protons

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Table IV. Positional Parameters and Their Estimated Standard Deviations for Structure **3**

atom	*x*	*y*	*z*
	Structure **3a**		
Tc′	−0.19926 (7)	0.04839 (6)	0.61334 (5)
Br′	−0.2879 (1)	0.13660 (8)	0.68717 (7)
N1F′	−0.2060 (7)	0.1472 (5)	0.5551 (5)
N2F′	−0.3409 (6)	−0.0085 (5)	0.6133 (4)
N3F′	−0.2360 (7)	0.0084 (5)	0.5136 (4)
N1B′	−0.0696 (6)	0.1095 (5)	0.6510 (4)
N2B′	−0.1804 (7)	−0.0192 (5)	0.6990 (4)
N3B′	−0.0841 (7)	−0.0223 (5)	0.5960 (4)
O1F′	−0.2828 (6)	0.1659 (5)	0.4999 (4)
O2F′	−0.4295 (6)	−0.0007 (5)	0.5624 (4)
O3F′	−0.3250 (6)	0.0325 (5)	0.4741 (4)
O1B′	0.0046 (5)	0.0832 (4)	0.7034 (4)
O2B′	−0.0871 (5)	−0.0223 (4)	0.7430 (3)
O3B′	0.0010 (5)	−0.0359 (4)	0.6459 (4)
B′	0.005 (1)	0.0015 (8)	0.7128 (7)
C11′	−0.142 (1)	0.2740 (7)	0.5432 (7)
C12′	−0.1394 (8)	0.1992 (6)	0.5756 (6)
C13′	−0.0588 (8)	0.1765 (6)	0.6327 (5)
C14′	0.0238 (9)	0.2258 (7)	0.6683 (6)
C21′	−0.454 (1)	−0.0770 (8)	0.6755 (7)
C22′	−0.3515 (8)	−0.0452 (7)	0.6683 (5)
C23′	−0.2584 (8)	−0.0493 (7)	0.7179 (5)
C24′	−0.250 (1)	−0.0854 (8)	0.7862 (7)
C31′	−0.203 (1)	−0.0696 (7)	0.4185 (6)
C32′	−0.1764 (8)	−0.0394 (6)	0.4907 (5)
C33′	−0.0861 (8)	−0.0591 (6)	0.5397 (5)
C34′	−0.0060 (9)	−0.1120 (7)	0.5270 (6)
C41′	0.1130 (9)	−0.0185 (7)	0.7619 (6)
C42′	0.119 (1)	−0.104 (1)	0.7799 (8)
C43′	0.222 (2)	−0.138 (1)	0.796 (1)
C43A′	0.166	−0.145	0.741
C44′	0.267 (1)	−0.140 (1)	0.7243 (9)
	Structure **3b**		
Tc	0.24192 (8)	0.16645 (6)	0.93435 (5)
Br	0.1555 (1)	0.20510 (8)	1.03517 (7)
N1F	0.3312 (7)	0.2627 (5)	0.9670 (5)
N2F	0.0898 (7)	0.1887 (6)	0.8792 (4)
N3F	0.2668 (7)	0.2115 (5)	0.8428 (5)
N1B	0.3579 (7)	0.1347 (5)	1.0119 (4)
N2B	0.1573 (6)	0.0717 (5)	0.9379 (5)
N3B	0.3182 (7)	0.0915 (5)	0.8854 (5)
O1F	0.3092 (7)	0.3320 (4)	0.9409 (4)
O2F	0.0552 (7)	0.2538 (5)	0.8510 (4)
O3F	0.2332 (7)	0.2809 (5)	0.8262 (4)
O1B	0.3666 (6)	0.0632 (4)	1.0348 (4)
O2B	0.2024 (6)	0.0094 (4)	0.9708 (4)
O3B	0.3495 (6)	0.0241 (4)	0.9143 (4)
B	0.318 (1)	0.0068 (9)	0.9807 (8)
C11	0.462 (1)	0.3229 (8)	1.0522 (7)
C12	0.4012 (8)	0.2571 (7)	1.0219 (6)
C13	0.4169 (8)	0.1828 (7)	1.0488 (6)
C14	0.492 (1)	0.1639 (8)	1.1126 (7)
C21	−0.093 (1)	0.1490 (9)	0.8494 (7)
C22	0.0189 (9)	0.1381 (8)	0.8800 (6)
C23	0.0595 (8)	0.0697 (7)	0.9126 (6)
C24	−0.007 (1)	0.0016 (9)	0.9147 (6)
C31	0.332 (1)	0.2051 (8)	0.7355 (6)
C32	0.313 (1)	0.1740 (7)	0.8010 (6)
C33	0.3440 (8)	0.1030 (7)	0.8263 (6)
C34	0.399 (1)	0.0485 (8)	0.7904 (7)
C41	0.364 (1)	−0.0733 (8)	1.0059 (7)
C42	0.348 (1)	−0.0984 (8)	1.0741 (7)
C43	0.410 (1)	−0.179 (1)	1.0865 (8)
C44	0.387 (1)	−0.206 (1)	1.1484 (9)

Table V. Positional Parameters and Their Estimated Standard Deviations for Structure **5**

atom	*x*	*y*	*z*
Tc	0.71010 (5)	0.41066 (9)	0.14878 (6)
Br	0.74954 (7)	0.4964 (1)	0.06883 (8)
N1F	0.6770 (5)	0.5602 (8)	0.1397 (6)
N2F	0.8104 (4)	0.3906 (8)	0.2343 (5)
N3F	0.7246 (5)	0.4316 (9)	0.2622 (5)
N1B	0.6199 (4)	0.4189 (8)	0.0380 (5)
N2B	0.7345 (4)	0.2832 (7)	0.1151 (5)
N3B	0.6618 (4)	0.3018 (7)	0.1649 (5)
O1F	0.7091 (5)	0.6334 (7)	0.1968 (5)
O2F	0.8529 (4)	0.4495 (8)	0.3011 (5)
O3F	0.7626 (4)	0.5088 (7)	0.3096 (5)
O1B	0.5926 (4)	0.3393 (6)	−0.0122 (5)
O2B	0.6882 (3)	0.2288 (6)	0.0482 (4)
O3B	0.6250 (4)	0.2300 (6)	0.1065 (5)
C11	0.6013 (8)	0.694 (1)	0.0462 (9)
C12	0.6240 (6)	0.583 (1)	0.0673 (7)
C13	0.5919 (5)	0.504 (1)	0.0100 (7)
C14	0.5292 (7)	0.514 (1)	−0.0763 (9)
C15	0.5153 (7)	0.629 (1)	−0.0943 (8)
C16	0.5344 (7)	0.696 (1)	−0.0323 (8)
C21	0.9094 (6)	0.301 (1)	0.2731 (8)
C22	0.8374 (5)	0.321 (1)	0.2201 (6)
C23	0.7937 (6)	0.256 (1)	0.1509 (6)
C24	0.8125 (5)	0.168 (1)	0.1236 (7)
C25	0.8849 (7)	0.149 (1)	0.1792 (8)
C26	0.9230 (7)	0.200 (1)	0.2522 (9)
C31	0.7145 (7)	0.380 (1)	0.3762 (7)
C32	0.7012 (6)	0.369 (1)	0.2900 (7)
C33	0.6657 (6)	0.292 (1)	0.2334 (7)
C34	0.6329 (6)	0.211 (1)	0.2496 (7)
C35	0.6302 (7)	0.240 (1)	0.3241 (8)
C36	0.6877 (7)	0.282 (1)	0.3908 (8)
B	0.6213 (7)	0.240 (1)	0.0263 (8)
C41	0.5759 (6)	0.155 (1)	−0.0373 (8)
C42	0.6083 (9)	0.051 (2)	−0.010 (1)
C43	0.5725 (9)	−0.041 (2)	−0.066 (1)
C44	0.5437 (9)	−0.030 (2)	−0.139 (1)
C42′	0.580	0.059	0.010
C43′	0.530	−0.025	−0.054
C44′	0.513	−0.038	−0.109

Table VI. Proton Magnetic Resonance Data for Complexes **2** and **3**

chem shift[a]	assignt
$TcCl(CDO)_3BCH_3$ (**2**)	
0.25 (s) [3]	B–CH_3
1.75 (m) [12]	β-protons, CDO
2.85 (m) [8]	α-protons, CDO ring 2[b]
3.1 (m) [4]	α-protons, CDO ring 1[b]
14.8 (s) [2]	O–H–O–H–O bridge
$TcBr(DMG)_3BC_4H_9$ (**3**)	
0.78 (t) [2]	B–CH_2
0.93 (t) [3]	–CH_3
1.44 (m) [4]	–CH_2CH_2
2.34 (s) [3]	CH_3[c]
2.38 (s) [6]	CH_3[d]
2.39 (s) [6]	CH_3[d]
2.43 (s) [3]	CH_3[c]
15.09 (s) [2]	O–H–O–H–O bridge

[a] NMR spectra were measured at 30 °C, in $CDCl_3$. Chemical shifts are given in ppm relative to tetramethylsilane with relative intensities in square brackets. Key: t = triplet, m = unresolved multiplet, s = singlet. [b] CDO ring 1 = unique ring; CDO ring 2 = the two equivalent CDO rings. [c] Methyl groups of unique DMG. [d] Methyl groups of two equivalent DMG groups.

on the carbon bound to the shielding boron atom are observed furthest upfield. The remainder of the butyl resonances are typical for alkyl groups. The lowest field signals are assigned to the two hydroxyl protons (vide infra).

Structural Results. The heptacoordinate technetium atom is surrounded by a hexadentate ligand and is also bonded to a halogen atom. The ligand consists of three bidentate dioxime groups joined through three covalent B–O bonds to a tetrahedral boron cap derived from methyl- or butylboronic acid. The average Tc–N distance in **3** is 2.08 Å, typical for Tc compounds.[24] The bidentate bite angle for each dioxime group is essentially constant (average = 72°), though smaller than the bite angle in the previously reported biscapped tris(dioxime) complexes (**7**: [Co^{II}-

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(24) Jurrison, S.; Dancey, K.; McPartlin, M.; Tasker, P. A.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 4743.

Table VII. Selected Bond Distances (Å) for Compounds **3** and **5**

	3a	**3b**	**5**
Tc–Br	2.586 (2)	2.576 (2)	2.567 (3)
Tc–N1F	2.121 (9)	2.13 (1)	2.14 (1)
Tc–N2F	2.126 (9)	2.131 (8)	2.113 (8)
Tc–N3F	2.079 (8)	2.07 (1)	2.06 (1)
Tc–N1B	2.051 (8)	2.037 (8)	2.067 (7)
Tc–N2B	2.072 (9)	2.051 (9)	2.05 (1)
Tc–N3B	2.059 (9)	2.04 (1)	2.04 (1)

Table VIII. Selected Bond Angles (deg) for **3** and **5**

	3a	**3b**	**5**
Br–Tc–N1F	79.2 (3)	80.8 (3)	78.4 (4)
Br–Tc–N2F	79.1 (3)	80.8 (3)	80.2 (3)
Br–Tc–N3F	134.9 (3)	137.7 (3)	135.2 (3)
Br–Tc–N1B	83.9 (3)	82.2 (3)	85.2 (4)
Br–Tc–N2B	84.0 (3)	83.1 (3)	83.2 (3)
Br–Tc–N3B	154.2 (2)	151.5 (3)	153.3 (3)
N1F–Tc–N1B	72.1 (3)	73.1 (4)	73.6 (4)
N2F–Tc–N2B	71.7 (3)	73.3 (4)	72.7 (4)
N3F–Tc–N3B	70.9 (3)	70.8 (4)	71.5 (4)
N1F–Tc–N2F	117.3 (3)	114.4 (4)	114.9 (4)
N1F–Tc–N3F	78.2 (4)	77.2 (4)	77.4 (4)
N2F–Tc–N3F	77.5 (4)	76.2 (4)	76.7 (4)
N1B–Tc–N2B	93.1 (3)	94.2 (4)	93.5 (4)
N1B–Tc–N3B	78.9 (3)	78.9 (4)	78.6 (4)
N2B–Tc–N3B	78.0 (4)	77.2 (4)	76.8 (5)

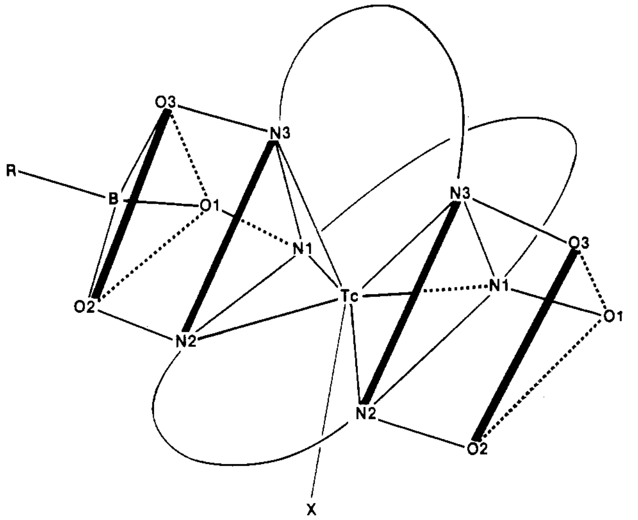
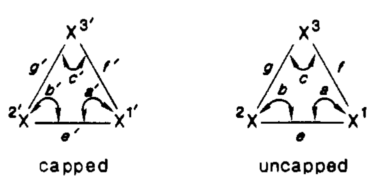


Figure 3. Oxygen and nitrogen triangles of the hexadentate ligand system of compounds **1–6**.

$(DMG)_3(BF)_2]$,[25] average = 76°; $[Co^{III}(DMG)_3(BF)_2]$,[25] average = 80°). Selected distances and angles are given in Tables VII and VIII, respectively.

The six ligating nitrogen atoms form a monocapped distorted trigonal prism, which can be characterized by the geometry of the triangles of nitrogen or oxygen atoms at the capped and uncapped ends of the complexes (See Figure 3 and Table IX). These triangles are nearly parallel (dihedral angles range from 0–3°). Triangles at the capped end are smaller than the corresponding triangles at the uncapped end due to the "pinching" constraints of the cap (the average Tc–N distance at the capped end is ~0.1 Å smaller than the average Tc–N distance at the uncapped end). Distortions from the strict trigonal symmetry of biscapped structures (e.g. $[Co^{II}(DMG)_3(BF_2)]$ (**7**) (Figure 4)) are due, at least in part, to the seventh halogen ligand: the two dioxime groups flanking the halogen are spread away from the halogen by ~20° toward the third dioxime group.[26] Consequently, the uncapped oxygen triangle is *isosceles* with two short sides (2.50 Å), which are suggestive of two strong *intra*molecular hydrogen bonds. Further evidence for these "hydrogen bridges" is seen in the proton NMR data (Table VI) and fast atom bombardment (FAB) mass spectral data.

Table IX. Geometry of Oxygen and Nitrogen Triangles



	structure			
	3		**7**	
param[a]	X = O	X = N	X = O	X = N
a, deg	40	47		
b, deg	40	47		
c, deg	100	86		
e, Å	3.83	3.61		
f, Å	2.49	2.64		
g, Å	2.51	2.62		
a′, deg	59	54	60	60
b′, deg	60	55	60	60
c′, deg	61	71	60	60
e′, Å	2.48	3.00	2.46	2.69
f′, Å	2.45	2.60	2.46	2.69
g′, Å	2.44	2.58	2.46	2.69
ϕ_1,[b] deg	40	17	-6	-8
ϕ_2,[b] deg	-37	-16	-6	-9
ϕ_3,[b] deg	0	0	-6	-9

[a] Errors in lengths are ~0.01 Å; errors in angles are ~0.3°. [b] Torsional angles, ϕ_i (=X*i*–Q–Q′–X*i*′ where Q and Q′ are the centroids of the uncapped and capped triangles), define the relative twist of the capped and uncapped triangles (ϕ_i = 0° for trigonal-prismatic structures; ϕ_i = 60° for octahedral structures).

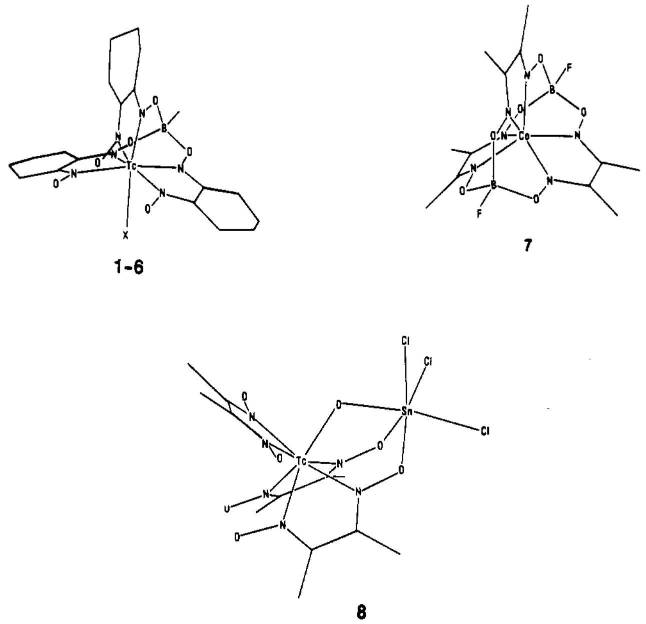


Figure 4. Comparison of mono- and biscapped complexes.

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(25) Zakrzewski, G. A.; Ghilardi, C. A.; Lingafelter, E. D. *J. Am. Chem. Soc.* **1971**, *93*, 4411.

(26) A similar spreading effect is seen in a decacoordinate lanthanide polyether complex,[27] where two halogen ligands spread three bidentate 1,2-diol groups. In this connection, it is of interest that acetonitrile in the crystal structure of the encapsulated complex Co(PccBF)[28] approaches the Co in a direction analogous to the Tc–X bond of the BATO structures. However, the intermolecular approach is weak (Co- -N = 3.96 Å) and does not distort the 3-fold symmetry of the complex.

(27) Benetollo, F.; Bonbieri, G.; DePaoli, G.; Hughes, D. L.; Parsons, D. G.; Truter, M. R. *J. Chem. Soc., Chem. Commun.* **1984**, 425.

(28) Churchill, M. R.; Reis, A. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1570.

The NMR resonance at 15 ppm, assigned to these bridging protons, disappears on addition of D_2O to the sample while all other resonances remain unchanged. This downfield chemical shift value is consistent with the trend observed for various bridging O--H--O protons in α-amine oxime complexes.[29] The positive FAB mass spectrum of **3** shows both the molecular ion at m/z 590/592 and the protonated molecular ion at m/z 591/593. When acidic (0.1 N DCl/D_2O) deuterated glycerol is used as the FAB matrix, the deprotonated molecular ion at m/z 589/591 is shifted to m/z 590/592. As this ion is most likely formed by the loss of an exchanged deuterium, the results are consistent with the presence of two exchangeable hydrogens. Positive FAB mass spectra allow a similar interpretation showing a 2 Da shift for the less intense M^+ parent.[15]

The long distance of the uncapped oxygen triangle (3.83 Å) precludes any hydrogen bonding between the two flanking oxygen atoms and apparently also precludes further capping by boron for, as previously mentioned, attempts to "force" the introduction of a second cap were unsuccessful.

One other tris(dioxime) Tc complex, **8**, was reported previously.[30] The technetium is seven-coordinate, bound to three DMG groups and a bridging oxygen atom. The oxygen atoms on one end of *two* of the DMG groups and the lone oxygen atom are joined through a Sn cap. Unlike the BATO complexes, however, the third DMG group is transversely disposed and not joined to the cap (Figure 4). Although these compounds are unique as monocapped vicinal dioxime complexes, seven-coordinate technetium(III) compounds have previously been reported with a variety of ligands. (See, for example, ref 31–33.)

Lability of the Halogen. The lability of the halogen ligand is predicted by X-ray photoelectron spectroscopy data,[34] which imply a charge separation in the Tc–Cl bond. The range of Cl $2P_{3/2}$ binding energies of technetium compounds is about 195.7 (Cl^-) to 198.2 eV (covalent Cl). An intermediate value, 197.1 eV, was found for both **2** and **4**. The halogen can be readily exchanged for another halogen or for hydroxide. The bromo complexes can be converted to the chloro complexes by stirring with excess chloride, either 1 M HCl or NaCl, in acetonitrile/water. In the presence of added base, the hydroxide derivative is obtained. Heating reduces to minutes the time required for reaction. Alternatively, the use of Ag^+ to abstract the bromide ion and subsequent addition of chloride ion under acidic conditions (HCl) result in quantitative conversion. Ag^+ may also be used to abstract the halide under basic conditions, to give the hydroxide derivative.

Attempts to remove the halogen and form a monocapped (or biscapped) hexacoordinate BATO complex were not successful. The use of Ag^+ to abstract the halogen gave only a monocapped hydroxide derivative, even when excess boronic acid was added to favor the formation of a biscapped complex.

Conclusion

A new family of technetium complexes has been isolated. The Tc(III) is surrounded by three dioxime molecules capped on one end by a boron–alkyl group. The dioxime oxygen atoms at the other, uncapped, end of the molecule are involved in hydrogen bonding with two protons. A halogen, which is easily exchanged for another halide or hydroxide, is also bonded to the seven-coordinate technetium atom. Structural distortions due to the presence of this halogen probably preclude the addition of a second boron cap.

These BATO complexes are prepared by template synthesis; consequently, a large number of complexes can be examined in vivo simply by changing the components of the ligand system. This is much easier than "traditional" preparations of ^{99m}Tc radiopharmaceuticals where pertechnetate and a reducing agent are added to a preformed ligand and the preparation of a different radiopharmaceutical first requires the synthesis of a new ligand.

The single cap of the BATO compounds also represents a distinct advantage in the study of radiopharmaceutical compounds, for better control and organ targeting of the ^{99m}Tc complex can be achieved by introducing only a single modification (the boron R group), as opposed to the multiple modifications that are introduced when derivatized bi- or tridentate ligands are bound to the technetium.

Acknowledgment. We wish to thank Dr. S. Jurisson and Dr. K. Linder for helpful discussions. We are grateful to Dr. Linder for experimental assistance.

Supplementary Material Available: Tables SI–SIII, SV–SVII, and SIX–XI, listing bond distances and angles and thermal parameters for **1**, **3**, and **5**, and Table SXIII, listing calculated hydrogen atom coordinates for **3** (18 pages); Tables SIV, SVIII, and SXII, listing observed and calculated structure factors for **1**, **3**, and **5** (33 pages). Ordering information is given on any current masthead page.

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Chemistry of Bis(platinum) Complexes. Formation of Trans Derivatives from Tetraamine Complexes

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Received December 20, 1988

Some chemistry of bis(platinum) complexes, and particularly the formation of complexes of the general formula $[\{trans\text{-}PtCl_2(NH_3)\}_2H_2N(CH_2)_nNH_2]$, is reported. The complexes contain both platinum coordination spheres in the trans configuration and are derived from the doubly bridged tetraamine complexes $[\{cis\text{-}Pt(NH_3)_2(H_2N(CH_2)_nNH_2)\}_2]Cl_4$. These latter complexes are derived in turn from $[PtCl_2(NH_3)_2]$ by reaction with the appropriate diamine in aqueous solution. A further set of tetraamine complexes may be prepared by the reaction of aqueous ammonia with $[\{cis\text{-}PtCl_2(NH_3)\}_2H_2N(CH_2)_nNH_2]$, giving $[\{Pt(NH_3)_3\}_2H_2N(CH_2)_nNH_2]Cl_4$. The complexes were characterized by IR and NMR (^{1}H, ^{13}C, ^{195}Pt) spectroscopy and elemental analyses. Kinetic measurements of the initial reaction of bis(platinum) complexes in DMSO indicate that the complexes are kinetically more reactive than their monomer analogues. The mechanism of the formation of the trans derivatives is discussed.

Bis(platinum) complexes containing two units of the antitumor drug Cisplatin, *cis*-$[PtCl_2(NH_3)_2]$, are of both chemical and biological interest, and their synthesis and initial DNA-binding properties have been reported.[1] Monomeric platinum–amine

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