An unexpected by-product obtained during the preparation of technetium(III) boronic acid adducts of dioximes. The single crystal structure of TcCl(DMG)$_2$(BDI)BEt (DMG = dimethylglyoxime, BDI = butane-2,3-dione imine-oxime)*

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Abstract

An unusual Tc(III) boron-capped imine-oxime complex has been isolated from the reaction of $^{99}TcCl_3(CH_3CN)(PPh_3)_2$, dimethyl glyoxime (DMG) and ethyl boronic acid ($EtB(OH)_2$). A single crystal X-ray structure analysis of this molecule $^{99}TcCl(DMG)_2(BDI)BEt$ (BDI = butane-2,3-dione imine-oxime) shows it to be seven coordinate: $TcClC_{14}H_{25}N_6O_5B$, $a = 9.073(2)$, $b = 23.686(5)$, $c = 19.539(6)$ Å; $\beta = 93.77(2)°$, $P2_1/n$, $Z = 8$. Its structure is very similar to that of previously reported Tc(III) complexes $^{99}TcCl(dioxime)_3BR$, except that one dioxime ligand on the molecule has been reduced to an imine-oxime.

Introduction

Boronic acid adducts of technetium dioximes (BATOs) are neutral, lipophilic complexes, which are formed by a template reaction involving a vicinal dioxime, a boronic acid, pertechnetate and stannous ion (as reductant) at low pH [1]. BATOs are seven-coordinate Tc(III) complexes, in which the technetium atom is bound to the nitrogens from three dioxime ligands; the remaining coordination site is filled by a monodentate, anionic ligand (for example, halide or hydroxide). The boronic acid caps one end of the tris-oxime complex (see Fig. 1). By varying the nature of the dioximes, boronic acid and the monodentate axial ligand, a large number of BATOs were synthesized, and their potential for use as radiopharmaceuticals was determined [2]. From this series, two compounds were selected for clinical evaluation [3–6], and one complex, TcCl(CDO)$_3$MeB (Cardiotec^{TM}) has been approved by the FDA for myocardial perfusion imaging.

While pertechnetate is the preferred starting material for the preparation of most BATO complexes, we have also conducted studies to investigate whether other, pre-reduced technetium compounds may be used. Recent reports have suggested that the Tc(III) complex $TcCl_3(CH_3CN)(PPh_3)_2$ is a versatile starting material for low oxidation state technetium complexes [7, 8]. We have found that the rhenium analog, $ReCl_3(CH_3CN)(PPh_3)_2$ is the preferred starting material for the preparation of rhenium analogs to the BATOs [ReCl(dioxime)$_3$BR] [9].

As reported here, BATOs can be produced in low yield from $TcCl_3(CH_3CN)(PPh_3)_2$. However, an unusual BATO-like imine-oxime complex is also obtained. We report here on the characterization and X-ray analysis of one of these by-products [TcCl(DMG)$_2$(BDI)BEt] (DMG = dimethyl glyoxime, BDI = butane-2,3-dione imine-oxime) and compare it to the analogous BATO complexes TcCl(DMG)$_3$BEt and TcCl(DMG)$_3$BMe [10]. The synthesis and characterization of several imine-containing Tc Schiff base complexes have been reported previously [11–16]. Technetium complexes containing aromatic imine ligands such as phenanthroline and bipyridine have also been described [8, 17–19]. However, to our knowledge, this is the first Tc complex reported to contain a primary imine ligand (C=NH).

Experimental

Materials and reagents

Dimethylglyoxime (DMG) (Eastern Chemicals) was used as received. Ammonium pertechnetate

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(NH_4TcO_4) was purchased from Oak Ridge National Laboratories and recrystallized from dilute aqueous hydrogen peroxide. ^{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. The complex $^{99}TcCl_3(CH_3CN)(PPh_3)_2$ was prepared as described previously [7]. All other chemicals were of reagent grade and were used as received. All solvents were of either HPLC or reagent grade (except acetonitrile, which was pesticide grade) and were used as received. All water used in these studies was obtained from a Millipore Milli-Q water purification unit.

Syntheses of $^{99}TcCl(DMG)_2(BDI)BEt$ and $^{99}TcCl(DMG)_3BEt$ from $^{99}TcCl_3(CH_3CN)(PPh_3)_2$

To $^{99}TcCl_3(CH_3CN)(PPh_3)_2$ (156 mg, 0.20 mmol) in 15 ml of N_2 purged ethanol were added DMG (117 mg, 1.0 mmol) and $(OH)_2BEt$ (50 mg, 0.68 mmol). This mixture was refluxed under N_2 for 1 h, during which time all starting material dissolved. The resulting red–brown solution was cooled to room temperature, treated with 15 ml of 1 N HCl, and the desired products extracted into 2×20 ml of CH_2Cl_2. The organic phase was back extracted with 15 ml of H_2O, dried over Na_2SO_4, filtered and evaporated. The brown oil was redissolved in a minimal volume of CH_2Cl_2 and purified on a 1.5×5 cm silica gel column (flash grade). Elution with CH_2Cl_2 removed emerald green $TcCl_4(PPh_3)_2$, unreacted starting material and the BATO complex $TcCl(DMG)_3BEt$. The imine-oxime complex was then removed from the column as a red band with 20% CH_3CN/80% CH_2Cl_2. Solvent was removed by rotary evaporation, and the complex was dissolved in 6 ml of CH_2Cl_2 and 1 ml of CH_3CN. Hexane was layered over the top and allowed to diffuse into the CH_2Cl_2 at room temperature over several days. Deep red–violet crystals of $TcCl(DMG)_2(BDI)BEt$ suitable for X-ray crystal structure analysis were formed. *Anal.* Calc. for $C_{14}H_{25}N_6O_5BClTc$: C, 33.45; H, 5.01; N, 16.72. Found: C, 33.15; H, 5.31; N, 16.60%.

The fractions containing the BATO complex $TcCl(DMG)_3BEt$ were also evaporated to dryness and were recrystallized from acetonitrile/1 N HCl. The $TcCl(DMG)_3BEt$ prepared in this fashion was identical to that prepared via tin reduction of pertechnetate (following procedures described elsewhere [10]) as determined by HPLC, TLC and UV–Vis spectroscopy. *Anal.* Calc. for $C_{14}H_{25}N_6O_6ClTc\cdot0.5H_2O$: C, 31.87; H, 4.97; N, 15.93. Found: C, 31.97; H, 4.76; N, 15.92%.

Crystal structure analysis

Unit cell parameters (see Table 1) were obtained through a least-squares analysis of fifteen high angle reflections. The space group assignment was confirmed by means of Weissenberg and precession photographs. The crystal density was measured by flotation in carbon tetrachloride/bromoform/hexane mixtures. Intensities were measured on a SYNTEX P21 diffractometer at 23 °C using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) with the θ–2θ variable-scan technique and were corrected for Lorentz polarization factors and for absorption [20]. Background counts were collected at the extremes of each scan. No decrease of intensity was observed during data collection. The structure was solved by heavy atom techniques and refined by full matrix least-squares analyses (SDP program package [21]) based on 'observed' reflections having $I \geqslant 3\sigma(I)$. Least-squares weights were assigned 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 refinements was $\Sigma_w(|F_o|-|F_c|)^2$. R is defined as $\Sigma||F_o|-|F_c||/\Sigma|F_o|$ while $R_w = [\Sigma_w(|F_o|-|F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$.

The approximate positions of most hydrogen atoms were evident in difference maps. All hydrogen atoms except the two on oxygens were introduced in fixed idealized positions for the final cycles of refinements. Residual intensities on the final difference map varied between 0.5 and −0.2 e/Å^3.

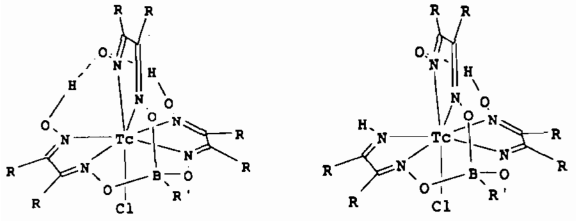
Results and discussion

Synthesis

When $^{99}TcCl_3(CH_3CN)(PPh_3)_2$, DMG and the boronic acid $(OH)_2BEt$ are refluxed under N_2 in ethanol, the BATO complex $^{99}TcCl(DMG)_3BEt$ and a less lipophilic side product $^{99}TcCl(DMG)_2(BDI)BEt$ are each formed in $\leqslant$30% yield. Considerable decomposition of the starting material occurs. The formation of the emerald green Tc(IV) complex $^{99}TcCl_4(PPh_3)_2$ [22] is also noted. The formation of the latter complex is increased if the reaction mixture is acidified with HCl. The BATO complex can be prepared in much higher yield from either $^{99}TcO_4^-$, $^{99}Tc(DMG)_3(\mu$-$OH)SnCl_3$ or $^{99}TcCl(DMG)_3$, following synthetic procedures outlined elsewhere [1, 10]. However, the yield of the imine-oxime complex, although low, has not been duplicated using other synthetic methods. The synthesis of the imine-oxime complex is general; we have used it to prepare several imine-oxime complexes of this class.

Crystal structure analysis

An X-ray crystal structure determination of the imine-oxime complex shows that this product is very close in structure to that of several BATO complexes that we have crystallographically characterized previously [1, 10] (Fig. 1), except that one of the uncapped oximes (C=N–OH) has been converted to an imine (C=NH). An ORTEP [23] diagram for TcCl(DMG)$_2$(BDI)BEt is shown in Fig. 2. Crystal data are given in Table 1, crystallographic atomic coordinates (excluding the hydrogen atoms) are given in Table 2, selected bond lengths in Table 3, and selected bond angles in Table 4. See also 'Supplementary material'. The two crystallographically independent molecules in the asymmetric unit of TcCl(DMG)$_2$(BDI)BEt have essentially identical structures.



In the BATO complex, technetium is bound to six nitrogen atoms, from three vicinal dioximes, and a monodentate anion (Cl$^-$ in this example). One end of the BATO is capped by a boronic acid. The uncapped oximes form two hydrogen bonds

In the imine-oxime complex, one of the uncapped oximes of the BATOs is reduced to an imine. Hydrogen bonding occurs only between the remaining pair of oximes

Fig. 1. General structures of (a) TcCl(dioxime)$_3$BR (BATOs) and (b) TcCl(dioxime)$_2$(butane-2,3-dione imine-oxime)BR complexes.

We have found that coordination about the technetium in the BATO complexes is distorted from trigonal prismatic geometry – the two 'equatorial' dioximes are bent away from the seventh (axial) ligand toward the unique 'apical' dioxime. At the uncapped end of the BATO, the hydrogen atoms of the equatorial oximes form two equivalent intramolecular hydrogen bonds (O---O = 2.534 Å) [1, 10] (Fig. 1(a)). Surprisingly, the absence of one of these hydrogen bonds (in TcCl(DMG)$_2$(BDI)BEt) does not lead to any substantial change in the mirror-symmetric molecular geometries of these complexes. The TcCl(DMG)$_2$(BDI)BEt complex and the BATOs have very similar heptacoordination geometries which appear to be relatively unaffected by the presence of hydrogen-bonded bridges.

Selected bond distances and angles for the two independent molecules of TcCl(DMG)$_2$(BDI)BEt are compared in Tables 3 and 4 to those previously observed for the structure of the BATO complex TcCl(DMG)$_3$BMe. As can be seen in Table 3, corresponding Tc–N distances in the two complexes are similar, with the largest difference (0.027 Å) involving the imine nitrogen N2F. The Tc–N (imine) bond

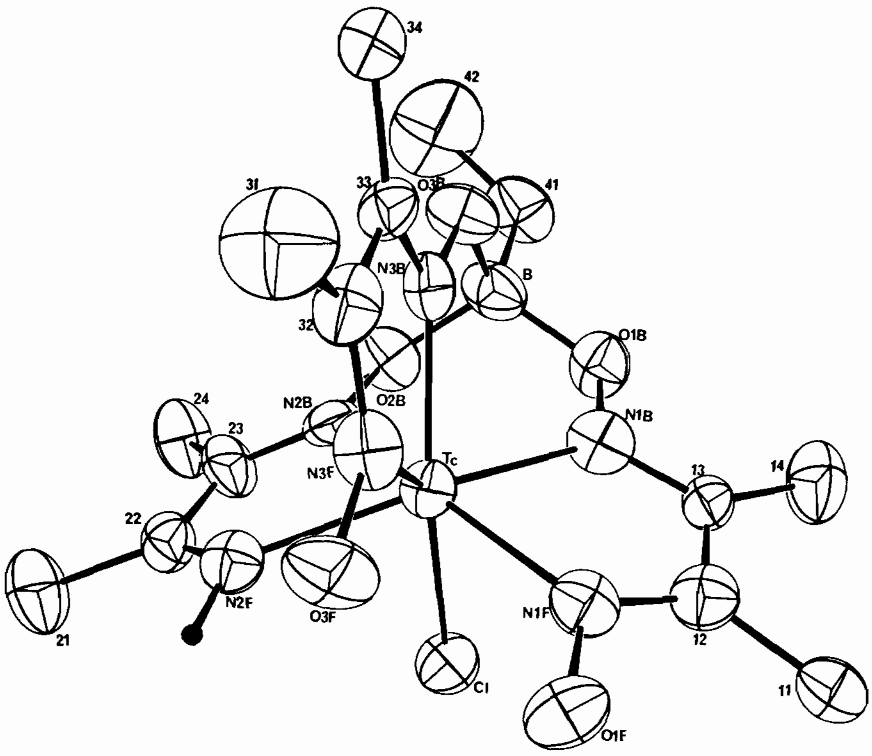


Fig. 2. ORTEP diagram of ^{99}TcCl(DMG)$_2$(butane-2,3-dione imine-oxime)BEt.

TABLE 1. Crystal data and structure refinement of $TcCl(DMG)_2(BDI)BEt$

Solvent	CH_2Cl_2/hexane
Color	violet
a (Å)	9.073(2)
b (Å)	23.686(5)
c (Å)	19.539(6)
β (°)	93.77(2)
V Å^3	4190(1)
Space group	$P2_1/n$
Z	8
D_{obs} (g cm^{-1})	1.60
D_{calc} (g cm^{-1})	1.590
Formula	$TcClC_{14}H_{25}N_6O_5B$
Formula weight	502.7
$2\theta_{\mathrm{max}}$ (°)	55
N_{ref}[a]	6946
N_{uni}[b]	6248
N_{obs}[c]	2636
N_{var}[d]	505
R	0.046
R_{w}	0.048

[a] Total no. of measured reflections within $2\theta_{\mathrm{max}}$. [b] Total no. of symmetry independent measured reflections. [c] Total no. of 'observed' reflections with $I \geqslant 3\sigma(I)$ used for refinements. [d] No. of variables in least-squares refinements.

distance falls within the range reported for technetium Schiff base [11–16] and aromatic imine [8, 17–19] complexes. The observed Tc–Cl bond distance (2.42 Å) in the imine-oxime complex is also very similar to that previously observed for other seven-coordinate tris dioxime complexes $TcCl(DMG)_3BMe$ (2.415(1) Å) and $TcCl(DMG)_3$ (2.411(1) Å).

Characterization

Table 5 lists UV–Vis, mass spectral, and HPLC data obtained for $TcCl(DMG)_2(BDI)BEt$ and $TcCl(DMG)_3BEt$. Mass spectral analysis of the BDI complex was carried out under both positive and negative FAB modes from a CH_2Cl_2/thioglycerol matrix. For the imine-oxime complex, under FAB (+) conditions, both molecular ion (M^{+}) and protonated molecular ion clusters $(M+H)^+$ were seen at m/e 502/504 and 503/505, respectively. The base peak in this spectrum was at m/z 467, which corresponds to the loss of HCl from the $(M+H)^+$ ion. Under negative FAB conditions, (M^{-}) and $(M-H)^-$ clusters are seen at 502/504 and 501/503. Again, the base peak of the spectrum is at 467 (loss of Cl). These fragmentation patterns are the same as those seen in the spectrum of BATO complexes [24]. However, all ions fall at 16 mass units lower than those of the parent BATO compound, consistent with the substitution of (C=NH) for (C=N–OH).

TABLE 2. Table of positional parameters for $TcCl(DMG)_2(BDI)BEt$

Atom	x	y	z	B (Å^2)
Tc1	0.2289(1)	0.48980(4)	0.69805(5)	2.84(2)
Cl1	0.4695(4)	0.4555(1)	0.7410(2)	4.05(8)
N1F	0.287(1)	0.4388(4)	0.6142(4)	3.4(2)
N1B	0.161(1)	0.4084(4)	0.7171(5)	3.6(2)
N2F	0.3413(9)	0.5672(4)	0.7078(4)	3.2(2)
N2B	0.2156(9)	0.5170(4)	0.7989(4)	3.1(2)
N3F	0.150(1)	0.5361(4)	0.6145(4)	3.2(2)
N3B	0.0074(9)	0.5023(3)	0.7051(4)	2.9(2)
O1F	0.3571(8)	0.4578(3)	0.5586(4)	4.2(2)
O1B	0.0908(9)	0.3959(3)	0.7755(4)	4.1(2)
O2B	0.1433(8)	0.4852(3)	0.8431(4)	4.2(2)
O3F	0.2443(8)	0.5523(3)	0.5680(4)	3.9(2)
O3B	−0.0679(8)	0.4798(3)	0.7592(4)	3.7(2)
C11	0.326(1)	0.3429(5)	0.5707(6)	4.1(3)
C12	0.272(1)	0.3849(5)	0.6191(6)	3.5(3)
C13	0.199(1)	0.3665(4)	0.6783(6)	3.1(3)
C14	0.170(2)	0.3063(5)	0.6963(7)	5.4(4)
C21	0.452(1)	0.6420(5)	0.7842(6)	4.8(3)
C22	0.366(1)	0.5887(5)	0.7676(6)	3.3(3)
C23	0.297(1)	0.5591(5)	0.8219(6)	3.8(3)
C24	0.307(1)	0.5748(5)	0.8968(6)	5.1(3)
C31	−0.048(1)	0.5896(6)	0.5490(6)	5.4(4)
C32	0.012(1)	0.5533(5)	0.6092(6)	3.4(3)
C33	−0.074(1)	0.5334(4)	0.6628(5)	2.8(3)
C34	−0.231(1)	0.5485(5)	0.6701(7)	4.1(3)
B1	0.027(2)	0.4455(6)	0.8099(8)	4.3(4)
C41	−0.072(1)	0.4232(6)	0.8681(6)	5.0(3)
C42	−0.156(2)	0.4665(8)	0.9052(9)	10.7(5)
Tc50	0.7117(1)	0.25648(4)	0.49954(5)	2.88(2)
Cl50	0.9707(3)	0.2710(1)	0.5324(2)	4.81(8)
N51F	0.804(1)	0.2327(4)	0.4072(5)	4.3(2)
N51B	0.7669(9)	0.1728(4)	0.5088(5)	3.3(2)
N52F	0.709(1)	0.3442(4)	0.5148(4)	3.1(2)
N52B	0.6927(9)	0.2697(4)	0.6024(4)	3.2(2)
N53F	0.560(1)	0.2853(4)	0.4244(5)	3.6(2)
N53B	0.515(1)	0.2189(4)	0.5134(4)	2.9(2)
O51F	0.826(1)	0.2695(4)	0.3537(4)	5.8(2)
O51B	0.7442(9)	0.1431(3)	0.5684(4)	4.5(2)
O52B	0.6859(8)	0.2238(3)	0.6454(4)	3.7(2)
O53F	0.6009(9)	0.3229(3)	0.3789(4)	4.5(2)
O53B	0.4952(8)	0.1810(3)	0.5664(4)	3.8(2)
C511	0.943(2)	0.1627(7)	0.3462(7)	6.7(4)
C512	0.858(1)	0.1817(5)	0.4043(6)	4.0(3)
C513	0.833(1)	0.1457(5)	0.4625(6)	4.0(3)
C514	0.877(2)	0.0862(6)	0.4638(8)	7.3(4)
C521	0.736(1)	0.4216(5)	0.5965(6)	4.2(3)
C522	0.720(1)	0.3614(5)	0.5779(6)	2.9(3)
C523	0.708(1)	0.3191(5)	0.6298(5)	3.1(3)
C524	0.720(1)	0.3289(5)	0.7045(6)	4.2(3)
C531	0.313(1)	0.2844(6)	0.3657(7)	5.6(4)
C532	0.425(1)	0.2653(5)	0.4196(5)	3.2(3)
C533	0.398(1)	0.2244(4)	0.4706(6)	3.1(3)
C534	0.263(1)	0.1926(5)	0.4766(6)	4.1(3)
B50	0.631(2)	0.1685(6)	0.6114(7)	3.5(3)
C541	0.593(1)	0.1285(5)	0.6704(6)	4.5(3)
C542	0.497(2)	0.1544(6)	0.7233(7)	5.9(4)

TABLE 3. Selected bond distances (Å) in TcCl(DMG)$_2$(BDI)BEt and TcCl(DMG)$_3$BMe

	TcCl(DMG)$_2$(BDI)BEt			TcCl(DMG)$_3$BMe[a]	Δ[b]
	Mol. 1	Mol. 2	Av.(d)[c]		
Tc–Cl	2.426(3)	2.419(3)	2.423(3)	2.415(1)	0.008
Tc–N1F	2.129(9)	2.115(9)	2.122(7)	2.120(5)	0.002
Tc–N2F[d]	2.100(9)	2.099(9)	2.100(1)	2.127(4)	−0.027
Tc–N3F	2.054(8)	2.063(9)	2.059(5)	2.062(3)	−0.003
Tc–N1B	2.064(9)	2.049(9)	2.057(7)	2.047(4)	0.010
Tc–N2B	2.084(8)	2.053(8)	2.069(15)	2.059(4)	0.010
Tc–N3B	2.046(8)	2.030(9)	2.038(8)	2.063(4)	−0.025
N1F–C12	1.29(1)	1.31(1)	1.30(1)	1.300(7)	0.00
N2F[d]–C22	1.28(1)	1.30(1)	1.29(1)	1.310(6)	−0.02
N3F–C32	1.32(1)	1.31(1)	1.31(1)	1.306(6)	0.00
N1F–O1F	1.37(1)	1.39(1)	1.38(1)	1.367(5)	0.01
N2F[d]–O2F				1.376(5)	
N3F–O3F	1.34(1)	1.34(1)	1.34(1)	1.345(6)	0.00
O1F–O3F	2.47(1)	2.48(1)	2.47(1)	2.494(6)	−0.02
O2F–O3F				2.559(4)	

[a] From ref. 10. [b] Δ = average value for TcCl(DMG)$_2$(BDI)BEt − value for TcCl(DMG)$_3$BMe. [c] d = average deviation. [d] Imine nitrogen.

TABLE 4. Selected bond angles (°) in TcCl(DMG)$_2$(BDI)BEt and TcCl(DMG)$_3$BMe

	TcCl(DMG)$_2$(BDI)BEt			TcCl(DMG)$_3$BMe[a]	Δ[b]
	Mol. 1	Mol. 2	Av.(d)[c]		
N1F–Tc–N1B	72.6(4)	73.1(4)	72.9(3)	72.9(2)	0.0
N2F[d]–Tc–N2B	72.7(3)	73.0(3)	72.9(2)	72.6(2)	0.3
N3F–Tc–N3B	71.6(3)	71.7(4)	71.7(1)	71.6(2)	0.1
N1B–Tc–Cl	84.0(3)	83.5(3)	83.8(3)	84.7(1)	−0.9
N1F–Tc–Cl	79.3(2)	80.3(3)	79.8(5)	79.1(1)	0.7
N2B–Tc–Cl	83.3(2)	82.0(2)	82.7(7)	83.0(1)	−0.3
N2F[d]–Tc–Cl	80.8(2)	81.0(3)	80.9(1)	80.6(1)	0.3
N3B–Tc–Cl	153.0(2)	151.0(3)	152.0(1)	152.6(9)	−0.6
N3F–Tc–Cl	135.3(3)	137.2(3)	136.3(9)	135.9(1)	0.4
N1F–C12–C13	115(1)	115(1)	115(0)	113.5(5)	1.5
C12–C13–N1B	112.9(9)	111(1)	112(1)	112.6(4)	−0.6
N2F[d]–C22–C23	115(1)	117(1)	116(1)	113.8(4)	2.2
C22–C23–N2B	112(1)	110.6(9)	111.3(7)	112.6(4)	−1.6

[a] From ref. 10. [b] Δ = average value for TcCl(DMG)$_2$(BDI)BEt − value for TcCl(DMG)$_3$BMe. [c] d = average deviation. [d] Imine nitrogen.

Deuterium exchange studies on TcCl(DMG)$_2$(BDI)BEt were carried out in a matrix of d^3-thioglycerol/D$_2$O. These studies indicated that the imine–oxime complex contains two exchangeable protons, as the (M^+) and (M+H)$^+$ peaks shifted to 504/506 and 505/507 on deuteration. Loss of DCl from the m/z 505 peak yields a strong base peak at 468. The bridging dioxime proton is expected to be freely exchangeable, from results previously obtained on deuterium exchanged BATO complexes [1, 24]. It appears, from the results obtained, that the imine NH proton is also capable of undergoing deuterium exchange.

Mechanism of formation

The mechanism of formation of the imine oxime ligand in TcCl(DMG)$_2$(BDI)BEt is not at all clear at this point. The starting dimethyl glyoxime was analytically pure, so formation of the BDI ligand had to take place either by reduction of dimethyl glyoxime in the reaction mixture, prior to coordination, or by modification of a coordinated DMG. It does not appear to be formed via decomposition of the tris-dioxime BATO complex, as treatment of isolated TcCl(DMG)$_3$BEt with refluxing mixtures of the solvents and reagents used for the synthesis of the imine-oxime complex, or with triphenyl phosphine

TABLE 5. UV–Vis, mass spectrometry and HPLC data for ^{99}TcCl(DMG)$_3$BEt and ^{99}TcCl(DMG)$_2$(butane-2,3-dione oxime-imine)BEt

Complex	*m*/*z*		λ_{max} in ACN	Retention time[a] (min)
	FAB$^+$	FAB$^-$		
TcCl(DMG)$_2$(BDI)BEt	502/504 $[M]^{\cdot +}$ 503/505 $[M+\mathrm{H}]^+$ 467 $[M+\mathrm{H}-\mathrm{HCl}]^+$	502/504 $[M]^{\cdot -}$ 501/503 $[M-\mathrm{H}]^-$ 467 $[M-\mathrm{Cl}]^-$	300, 320(sh), 384 480	2.04
TcCl(DMG)$_3$BEt	518/520 $[M]^{\cdot +}$ 519/521 $[M+\mathrm{H}]^+$ 483 $[M+\mathrm{H}-\mathrm{HCl}]^+$	518/520 $[M]^{\cdot -}$ 517/519 $[M-\mathrm{H}]^-$ 483 $[M-\mathrm{Cl}]^-$	280, 320, 384 456	2.40

[a] Column is Nucleosil C-8. 70/30 CH_3CN/0.1 M citric acid, pH 2.3, flow rate 1.5 ml/min.

under either acidic or basic conditions, did not cause the formation of the imine-oxime complex. It does seem likely, however, that the imine moiety forms at or near the time of coordination to technetium, as imine bonds (C=NH) are quite readily hydrolyzed to ketones under the reaction conditions used [25]. Interestingly, the coordinated imine functionality on TcCl(DMG)$_2$(BDI)BEt is quite water stable, even under strongly acidic conditions.

The triphenylphosphine present on the TcCl$_3$(CH$_3$CN)(PPh$_3$)$_2$ starting material may not be entirely innocent in this reaction, as addition of PPh$_3$ to freeze-dried kits for the preparation of ^{99m}Tc BATO complexes causes the formation of analogous imine-oxime complexes in low yield on the carrier free level [26]. However, PPh$_3$ is not essential for the synthesis of these imine-oxime complexes, as we have also noted their formation in ^{99m}Tc reaction mixtures that do not contain phosphines [27].

Supplementary material

Full crystallographic atomic coordinates, temperature factors, molecular geometry, and structure factors are available from the authors on request.

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