

# Investigations of technetium–organohydrazine coordination chemistry. The crystal and molecular structures of $[\text{TcCl}_2(\text{C}_8\text{H}_5\text{N}_4)(\text{PPh}_3)_2] \cdot 0.75\text{C}_7\text{H}_8$ and $[\text{TcNCl}_2(\text{PPh}_3)_2] \cdot 0.25\text{CH}_2\text{Cl}_2$

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## Abstract

Reaction of  $[\text{TcOCl}_4]^-$  with hydralazine·HCl in methanol at room temperature yields the Tc(V)–hydrazido(3–) complex  $[\text{Tc}(\text{C}_8\text{H}_5\text{N}_4)\text{Cl}_2(\text{PPh}_3)_2] \cdot 0.75\text{C}_7\text{H}_8$  (1). In contrast, the reaction in refluxing methylene chloride produces the Tc(V)–nitrido complex  $[\text{TcNCl}_2(\text{PPh}_3)_2] \cdot 0.25\text{CH}_2\text{Cl}_2$  (2). Crystal data. 1: triclinic  $P\bar{1}$ ,  $a = 11.592(3)$ ,  $b = 12.105(3)$ ,  $c = 17.884(4)$  Å,  $\alpha = 107.76(2)^\circ$ ,  $\beta = 99.03(2)^\circ$ ,  $\gamma = 106.11(2)^\circ$ ,  $V = 2232.7(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.40$  g/m<sup>3</sup>; structure solution and refinement based on 2623 reflections ( $F \geq 6\sigma(F_o)$ ); Mo K $\alpha$ ,  $\lambda = 0.71073$  Å) converged at  $R = 0.058$ . 2: monoclinic  $C2/c$ ,  $a = 24.081(9)$ ,  $b = 9.539(4)$ ,  $c = 15.650(6)$  Å,  $\beta = 116.18(1)^\circ$ ,  $V = 3226.8(11)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.37$  g/cm<sup>3</sup>; 3118 reflections;  $R = 0.052$ .

## Introduction

The dramatic development of the basic coordination chemistry of the synthetic radioactive element technetium in the past decade reflects its expanding application in the diagnostic imaging of internal organs by  $\gamma$ -scintillation detection [1, 2].  $^{99\text{m}}\text{Tc}$  remains the isotope of choice as a consequence of its reasonable cost, ready availability and optimal nuclear properties of high gamma energy (140 KeV) with no particulate emissions. In order to be considered as clinically useful radiopharmaceuticals, technetium complexes must be easily prepared, yielding a single radiochemically pure product, and stable under physiological conditions and must possess useful biodistribution properties. One approach has focussed on the binding of technetium to tumor localizing monoclonal and polyclonal antibodies [3–5].

Previous efforts directed toward the conjugation of  $^{99\text{m}}\text{Tc}$  to proteins include the use of bifunctionalized chelates, such as diethylenetriaminepentaacetic acid [6],  $\text{N}_2\text{S}_2$  and  $\text{N}_3\text{S}$  donor ligands [7–13] and direct reduction of the protein disulfide bonds

to form free sulfhydryl groups [14]. These methods have met with only limited success [14].

We have recently described a simple, efficient and general method for labelling proteins with  $^{99\text{m}}\text{Tc}$  based on bifunctional hydrazine reagents. The hydrazine protein conjugates react with  $^{99\text{m}}\text{Tc}$  glucoheptonate under mild conditions to give stable  $^{99\text{m}}\text{Tc}$  labelled proteins in >90% radiometric yield [15, 16].

However, the fundamental coordination chemistry of technetium with organohydrazine ligands remains largely unexplored [17–23], although that of its Group 7 congener Re has been extensively developed [24]. In order to gain some insight into the possible modes of attachment of technetium to the organohydrazine linker, we have undertaken extensive studies of the chemistry of various organohydrazines with this element using macroscopic quantities of the long-lived radionuclide  $^{99}\text{Tc}$ . The work has focussed on the chemistry of complex precursors with the Tc(V)–oxo core, similar to that present in the radiopharmaceutical preparations. In this paper we present the full details of the synthesis and structural investigation of  $[\text{TcCl}_2(\text{C}_8\text{H}_5\text{N}_4)(\text{PPh}_3)_2] \cdot 0.75\text{C}_7\text{H}_8$  [20] and report the synthesis of  $[\text{TcNCl}_2(\text{PPh}_3)_2]$  via dissociation of Tc–hydrazido species.

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## Experimental

**Caution:**  $^{99}\text{Tc}$  is a weak  $\beta$ -emitter. All work was performed in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere [25]. Solid ammonium [ $^{99}\text{Tc}$ ] pertechnetate was supplied by Oakridge National Laboratories, TN and was treated with 35%  $\text{H}_2\text{O}_2$  and standardized according to Boyd's method [26].  $[\text{TcCl}_4(\text{PPh}_3)_2]$  and  $[\text{TcOCl}_4][\text{n-Bu}_4\text{N}]$  were prepared according to literature procedures [27, 28]. Reagents and solvents used were of commercially available reagent grade quality and were dried according to published methods prior to their use. Preparations of the compounds were carried out under Ar using standard Schlenk techniques unless otherwise specified.

X-ray crystallographic studies were performed on a Nicolet R3m/V diffractometer adapted for low temperature collection.  $^1\text{H}$  NMR spectra were recorded on a Varian 300 MHz spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR; electronic spectra were recorded on a Shimadzu UV 160. Elemental analysis were performed by Atlantic Microlab, Atlanta, GA.

### Synthesis of $[\text{TcCl}_2(\text{C}_8\text{H}_5\text{N}_4)(\text{PPh}_3)_2] \cdot 0.75\text{C}_7\text{H}_8$ (**1**)

Addition of a solution of  $[(\text{n-C}_4\text{H}_9)_4\text{N}][\text{TcOCl}_4]$  (0.100 g, 0.2 mmol) in 2 ml of anhydrous methanol to a suspension of hydralazine-HCl (0.081 g, 0.4 mmol) (hydrazinophthalazine-HCl) in 2 ml of methanol resulted in a homogeneous red-brown solution. To this solution was added triphenylphosphine (0.324 g) in 15 ml of methanol, resulting in no observable color change. The final solution was refluxed for 2 min, cooled to room temperature, and chilled in an ice bath for 30 min. The dark brown crystalline precipitate was collected by vacuum filtration, redissolved into a minimum of  $\text{CH}_2\text{Cl}_2$  and filtered through a silica gel column using  $\text{CH}_2\text{Cl}_2$  as eluant. Pure crystalline complex was obtained upon evaporation of solvent. X-ray grade crystals were grown from solvent diffusion of toluene into a solution of the complex in  $\text{CH}_2\text{Cl}_2$ .

Yield: 25%. *Anal.* Calc. for  $\text{C}_{51}\text{H}_{44}\text{N}_4\text{P}_2\text{Cl}_2\text{Tc} \cdot \text{nC}_7\text{H}_8$ : C, 64.8; H, 4.69; N, 5.93. Found: C, 64.5; H, 4.52; N, 5.95%.

### Synthesis of $[\text{TcNCl}_2(\text{PPh}_3)_2] \cdot 0.25\text{CH}_2\text{Cl}_2$ (**2**)

**Method A.** A mixture of 1,1-diphenylhydrazine (55 mg; 0.3 mmol) and  $[\text{TcCl}_4(\text{PPh}_3)_2]$  (207 mg; 0.27 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$  was refluxed for 6 h. The resulting red-brown solution was filtered to remove some brown precipitate. The filtrate volume was

reduced to 20 ml and then layered with 45 ml toluene/ether mixture (2:1). After two weeks at room temperature, orange crystals were deposited at the interface of the two liquids. The crystals were collected, washed with ether and vacuum dried. Yield: 60%. *Anal.* Calc. for  $\text{C}_{36}\text{H}_{30}\text{NCl}_2\text{P}_2\text{Tc} \cdot 0.25\text{CH}_2\text{Cl}_2$ : C, 61.1; H, 4.27; N, 1.98. Found: C, 61.7; H, 4.25; N, 1.91%. IR (KBr,  $\text{cm}^{-1}$ ): 1480(m), 1435(s), 1260(w), 1075(s), 1085(s), 800(w), 740(vs), 700(m), 685(vs), 520(s), 495(s), 360(w), UV-Vis,  $\lambda_{\text{max}}$  in DMF ( $\epsilon$ ,  $\text{cm}^{-1}\text{M}^{-1}$ ): 275 (6383), 344 (3053), 387 (580), 463 (325).

**Method B.** Repeated exactly as described above except that dry hydralazine hydrochloride was used. Yield: 50%.

**Method C.** A methylene chloride solution of  $[(\text{n-C}_4\text{H}_9)_4\text{N}][\text{TcOCl}_4]$  (0.100 g, 0.2 mmol) and hydralazine-HCl (0.04 g, 0.2 mmol) was refluxed for 0.5 h. Addition of  $\text{PPh}_3$  followed by cooling overnight at  $-20^\circ\text{C}$  yielded orange crystals of **2**.

**Method D.** A solution of  $[\text{TcCl}_4(\text{PPh}_3)_2]$  (0.1 g, 0.13 mmol) and *N,N*-diphenylhydrazine (0.05 g, 0.26 mmol) in methanol (10 ml) was refluxed for 2 h in a flask open to the atmosphere. Concentration to 5 ml, followed by addition of either, yielded orange crystals of **2** in 25% yield.

### Synthesis of $[\text{Tc}(\text{NNMePh})\text{Cl}_3(\text{PPh}_3)_2]$ (**3**)

In a vessel open to the atmosphere, a solution of  $[\text{TcCl}_4(\text{PPh}_3)_2]$  (0.1 g, 0.13 mmol) and  $(\text{Me}_3\text{Si})_2\text{-NNMePh}$  (0.035 g, 0.13 mmol) was stirred for 4 h. Yellow orange crystals of **3** were obtained by careful layering of the reaction solution with ether, followed by standing at  $-20^\circ\text{C}$  for 3 weeks. *Anal.* Calc. for  $\text{C}_{43}\text{H}_{38}\text{N}_2\text{P}_2\text{Cl}_3\text{Tc}$ : C, 60.7; H, 4.47; N, 3.30. Found: C, 60.3; H, 4.26; N, 3.21%.

### X-ray crystallographic studies of $[\text{TcCl}_2(\text{C}_8\text{H}_5\text{N}_4)(\text{PPh}_3)_2] \cdot 0.75\text{C}_7\text{H}_8$ (**1**) and $[\text{TcNCl}_2(\text{PPh}_3)_2] \cdot 0.25\text{CH}_2\text{Cl}_2$ (**2**)

Crystal data and experimental parameters for the structure determinations of **1** and **2** are given in Table 1. Tables 2 and 3 list atomic positional parameters, while Tables 4 and 5 provide selected bond lengths and angles.

Green-violet dichroic crystals of **1** were grown from diffusion of toluene into a solution of **1** in  $\text{CH}_2\text{Cl}_2$  and mounted with a coating of epoxy to prevent crystal decay due to evaporation of lattice solvent. Dimensions of the crystal unit cell were determined from the centering of 25 reflections greater than  $15^\circ$  in  $2\theta$  and confirmed by axial pho-

TABLE 1. Summary of crystal data and experimental conditions for the X-ray crystallographic studies of  $[\text{Tc}(\text{C}_8\text{H}_5\text{N}_4)\text{Cl}_2(\text{PPh}_3)_2] \cdot 0.75\text{C}_7\text{H}_8$  (1) and  $[\text{TcNCl}_2(\text{PPh}_3)_2] \cdot 0.25\text{CH}_2\text{Cl}_2$  (2)

	1	2
<i>Crystal data</i>		
Empirical formula	$\text{C}_{49.25}\text{H}_{41}\text{N}_4\text{P}_2\text{Cl}_2\text{Tc}$	$\text{C}_{36.25}\text{H}_{30.5}\text{Cl}_{2.5}\text{NTc}$
Color; habit	green/violet parallelipeds	orange blocks
Crystal size (mm)	$0.21 \times 0.20 \times 0.32$	$0.15 \times 0.25 \times 0.20$
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions		
<i>a</i> (Å)	11.592(3)	24.081(9)
<i>b</i> (Å)	12.205(3)	9.539(4)
<i>c</i> (Å)	17.884(4)	15.650(6)
$\alpha$ (°)	107.76(2)	90.00
$\beta$ (°)	99.03(2)	116.18(1)
$\gamma$ (°)	106.11(2)	90.00
Volume (Å <sup>3</sup> )	2232.7(9)	3226.8(11)
Z	2	4
Formula weight	942.7	667.5
Density (calc.) (g/cm <sup>3</sup> )	1.402	1.37
Density (exp.) (g/cm <sup>3</sup> )	1.40(2)	1.34(2)
Absorption coefficient (cm <sup>-1</sup> )	5.44	7.31
<i>F</i> (000)	968.0	1330.5
<i>Data collection</i>		
Diffractometer	Nicolet R3m/V	Nicolet R3m/V
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
Temperature (K)	297	233
Monochromator	highly oriented graphite crystal	
$2\theta$ Range (°)	3.5–45.0	
Scan type	$2\theta$ - $\theta$	
Scan speed (°/min)	variable; 2.00–30.00	
Scan range ( $\omega$ )	1.20° plus K $\alpha$ -separation	
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time	
Standard reflections	3 measured every 98 reflections	
Reflections collected	6238	3270
Independent reflections	5887 ( $R_{\text{int}} = 2.29\%$ )	3169 ( $R_{\text{int}} = 3.01\%$ )
Observed reflections	2623 ( $F > 6.0\sigma(F)$ )	3118 ( $F > 6.0\sigma(F)$ )
Absorption correction	based on $\phi$ scans of 5 medium intensity reflections	
$T_{\text{max}}/T_{\text{min}}$	1.10	1.08
<i>Solution and refinement</i>		
System used	Nicolet SHELXTL PLUS (Micro VAX II)	
Solution	Patterson method	
Refinement method	full matrix least-squares	
Quantity minimized	$\sum w(F_o - F_c)^2$	
Hydrogen atoms	rigid model, fixed isotropic <i>U</i>	
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0011F^2$	$w^{-1} = \sigma^2(F) + 0.004F^2$
Final <i>R</i> indices (obs. data)	$R = 0.058$ $R = 0.056$	$R = 0.052$ $R = 0.052$
Goodness-of-fit	1.15	1.26
Largest and mean $\Delta/\sigma$	0.003, 0.000	0.004, 0.001
Data-to-parameter ratio	10.8:1	13.6:1
Largest difference peak (e Å <sup>-3</sup> )	0.68	0.42
Largest difference hole (e Å <sup>-3</sup> )	-0.48	-0.23

topographs. The quadrants  $+h$ ,  $+k$ ,  $\pm l$  were collected from 3.5 to 45° in  $2\theta$  using a  $\theta$ - $2\theta$  scan mode. The intensities of 3 check reflections measured every 98 reflections throughout the data collection showed no significant decay in crystal quality. Data were cor-

rected for absorption using  $\phi$ -scans of 5 medium intensity reflections with  $\phi$  in the ranges 75–85° and 260–265°. Of 6238 reflections collected 2623 reflections with  $F > 6\sigma(F)$  were used in the final structure refinement.

TABLE 2. Atomic positional parameters ( $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Tc}(\text{C}_8\text{H}_5\text{N}_4)\text{Cl}_2(\text{PPh}_3)_2] \cdot 0.75\text{C}_7\text{H}_8$  (**1**)

	x	y	z	$U_{\text{eq}}^a$
Tc(1)	2250(1)	1251(1)	2525(1)	26(1)
Cl(1)	4319(3)	1946(3)	3382(2)	41(2)
Cl(2)	2634(3)	193(3)	1291(2)	37(2)
P(1)	1902(3)	-662(3)	2822(2)	34(2)
C(2)	-326(8)	-2129(8)	3012(4)	51(4)
C(3)	-1564	-2913	2719	67(5)
C(4)	-2202	-3238	1910	81(5)
C(5)	-1602	-2778	1396	72(5)
C(6)	-364	-1993	1689	57(4)
C(1)	274	-1669	2498	37(3)
C(8)	1840(7)	342(8)	4425(5)	49(4)
C(9)	2101	534	5253	61(4)
C(10)	2871	-6	5569	67(5)
C(11)	3379	-739	5058	66(5)
C(12)	3117	-931	4230	54(4)
C(7)	2348	-391	3913	37(3)
C(14)	2049(6)	-2815(8)	1748(5)	67(5)
C(15)	2681	-3515	1335	75(5)
C916)	3976	-3048	1506	64(4)
C(17)	4639	-1880	2091	66(5)
C(18)	4007	-1180	2505	48(4)
C(13)	2712	-1648	2333	38(3)
P(2)	2801(3)	3141(3)	2210(2)	33(2)
C(20)	1039(8)	4332(7)	2210(4)	59(4)
C(21)	-38	4495	1867	69(5)
C(22)	-721	3749	1069	63(4)
C(23)	-327	2842	613	56(4)
C(24)	750	2679	957	41(4)
C(19)	1433	3424	1755	29(3)
C(31)	3589(7)	4671(6)	3867(5)	41(3)
C(32)	4204	5783	4518	50(4)
C(33)	4889	6807	4383	62(4)
C(34)	4958	6719	3596	56(4)
C(35)	4343	5607	2944	47(4)
C(36)	3658	4582	3080	36(3)
C(26)	3579(6)	3549(7)	846(5)	45(4)
C(27)	4441	3649	385	52(4)
C(28)	5540	3427	603	56(4)
C(29)	5776	3105	1281	66(5)
C(30)	4913	3005	1741	51(4)
C(25)	3815	3227	1524	34(3)
N(1)	1333(10)	1768(8)	3159(5)	34(5)
N(2)	210(10)	1722(9)	3097(6)	37(5)
N(3)	364(9)	707(9)	1820(6)	30(5)
N(4)	-104(9)	88(9)	990(6)	36(5)
C(40)	-402(12)	1052(11)	2271(8)	34(7)
C(41)	-1686(13)	799(11)	1927(8)	36(7)
C(42)	-2481(12)	1147(12)	2409(9)	45(7)
C(43)	-3716(13)	807(14)	2004(10)	61(10)
C(44)	-4172(13)	164(14)	1170(10)	58(8)
C(45)	-3404(13)	-174(12)	708(9)	47(7)
C(46)	-2147(11)	152(11)	1084(7)	33(6)
C(47)	-1275(12)	-145(12)	661(8)	41(7)
C(81)	9028(9)	4704(8)	3746(6)	66(5)
C(82)	7736	4376	3568	70(5)
C(83)	7198	5177	3988	67(5)
C(84)	7953	6306	4586	73(5)
C(85)	9245	6634	4764	69(5)
C(80)	9783	5833	4344	66(5)
C(86)	-1185(16)	3814(15)	5466(10)	97(6)

<sup>a</sup>Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

TABLE 3. Atomic positional parameters ( $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Tc}-\text{NCl}_2(\text{PPh}_3)_2] \cdot 0.25\text{C}_2\text{H}_2\text{Cl}_2$  (**2**)

	x	y	z	$U_{\text{eq}}^a$
Tc	0	2639(1)	2500	23(2)
P(1)	945(1)	3042(2)	2295(1)	25(1)
Cl(1)	549(1)	3484(2)	4083(1)	36(1)
N	0	960(8)	2500	27(4)
C(11)	894(3)	2487(7)	1151(4)	29(3)
C(12)	777(4)	1090(8)	920(6)	45(4)
C(13)	737(4)	571(8)	71(6)	51(4)
C(14)	804(4)	1450(8)	-572(5)	41(4)
C(15)	914(4)	2852(8)	-360(5)	41(3)
C(16)	962(3)	3380(7)	493(5)	35(3)
C(21)	1149(3)	4915(7)	2421(5)	29(3)
C(22)	1705(3)	5382(7)	3141(5)	37(3)
C(23)	1843(4)	6804(8)	3252(6)	47(4)
C(24)	1420(4)	7762(8)	2639(6)	51(4)
C(25)	872(4)	7288(8)	1935(7)	55(4)
C(26)	731(3)	5887(7)	1819(6)	40(3)
C(31)	1639(3)	2103(7)	3123(5)	29(3)
C(32)	1624(3)	1340(7)	3873(5)	32(3)
C(33)	2145(3)	600(8)	4482(5)	38(3)
C(34)	2673(4)	633(9)	4367(5)	46(3)
C(35)	2698(4)	1411(11)	3644(6)	61(4)
C(36)	2174(4)	2125(9)	3007(5)	49(4)

<sup>a</sup>Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Using the SHELXTL PLUS software package, the technetium atom was located from a Patterson solution and neutral atom scattering factors were used throughout refinement. The aromatic rings of the hydralazine ligand were refined as free anisotropic atoms; the phenyl rings of the triphenylphosphines were refined as idealized isotropic rigid groups. Although some hydrogen atoms were located, final hydrogen positions were calculated.

An orange block-shaped crystal of **2** taken directly from the mother liquor was placed on a glass fiber using epoxy resin and immediately bathed in a nitrogen stream at  $-40$  °C. All other conditions and details are similar to those noted above for **1**.

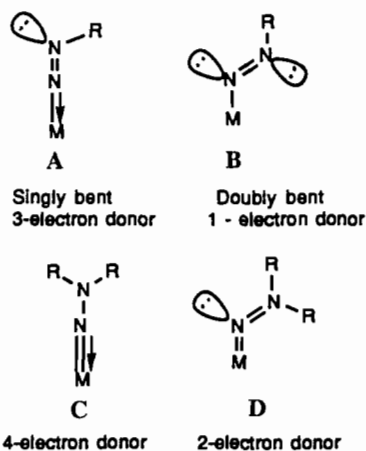
## Results and discussion

### Syntheses and spectroscopic properties

Although technetium has been shown to form multiple bonds with a variety of nitrogenous donor ligands, forming structurally characterized nitrido [29–39] and nitrosyl species [40], the coordination chemistry with organohydrazine ligands capable of stabilizing the Tc–diazenido cores (**A** or **B**) and the Tc–hydrazido cores (**C** or **D**) [41] has not been systematically developed.

TABLE 4. Selected bond lengths (Å) and angles (°) for [Tc(C<sub>8</sub>H<sub>5</sub>N<sub>4</sub>)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] $\cdot$ 0.75C<sub>7</sub>H<sub>8</sub> (1)

Tc(1)–Cl(1)	2.397(3)	Tc(1)–Cl(2)	2.371(3)
Tc(1)–P(1)	2.490(4)	Tc(1)–P(2)	2.477(4)
Tc(1)–N(1)	1.767(12)	Tc(1)–N(3)	2.151(9)
P(1)–C(1)	1.828(8)	P(1)–C(7)	1.838(10)
P(1)–C(13)	1.826(10)	P(2)–C(19)	1.834(10)
P(2)–C(36)	1.838(7)	P(2)–C(25)	1.833(9)
N(1)–N(2)	1.274(17)	N(2)–C(40)	1.403(15)
N(3)–N(4)	1.381(12)	N(3)–C(40)	1.357(19)
N(4)–C(47)	1.305(17)	C(40)–C(41)	1.425(20)
C(41)–C(42)	1.420(22)	C(41)–C(46)	1.403(16)
C(42)–C(43)	1.380(19)	C(43)–C(44)	1.388(21)
C(44)–C(45)	1.369(24)	C(45)–C(46)	1.394(18)
C(46)–C(47)	1.414(20)		
		Cl(1)–Tc(1)–Cl(2)	97.6(1)
Cl(1)–Tc(1)–P(1)	86.5(1)	Cl(2)–Tc(1)–P(1)	87.4(1)
Cl(1)–Tc(1)–P(2)	89.4(1)	Cl(2)–Tc(1)–P(2)	89.1(1)
P(1)–Tc(1)–P(2)	174.2(1)	Cl(1)–Tc(1)–N(1)	106.6(3)
Cl(2)–Tc(1)–N(1)	155.7(3)	P(1)–Tc(1)–N(1)	92.6(4)
P(2)–Tc(1)–N(1)	92.5(4)	Cl(1)–Tc(1)–N(3)	176.3(3)
Cl(2)–Tc(1)–N(3)	86.0(3)	P(1)–Tc(1)–N(3)	94.5(3)
P(2)–Tc(1)–N(3)	89.9(3)	N(1)–Tc(1)–N(3)	69.8(4)
Tc(1)–P(1)–C(1)	114.2(4)	Tc(1)–P(1)–C(7)	113.8(3)
Tc(1)–P(1)–C(13)	114.4(4)	Tc(1)–P(2)–C(19)	112.9(3)
Tc(1)–P(2)–C(36)	116.1(3)	Tc(1)–P(2)–C(25)	116.5(3)
Tc(1)–N(1)–N(2)	138.6(7)	N(1)–N(2)–C(40)	104.9(11)
Tc(1)–N(3)–N(4)	127.2(8)	Tc(1)–N(3)–C(40)	113.5(7)
N(4)–N(3)–C(40)	119.3(10)	N(3)–N(4)–C(47)	118.7(11)
N(2)–C(40)–N(3)	113.2(11)	N(2)–C(40)–C(41)	123.8(13)
N(3)–C(40)–C(41)	123.0(11)	C(40)–C(41)–C(46)	116.7(13)
C(41)–C(46)–C(47)	116.4(11)	N(4)–C(47)–C(46)	125.8(11)



Reactions of metal–oxo species with organohydrazine ligands generally proceed by condensation type reactions, resulting in displacement of the oxo groups as H<sub>2</sub>O and formation of the chemically robust metal–hydrazido (C) or metal–diazenido (A) unit [41–43]. In contrast, the chemistry of the Tc–oxo group appears to be complicated by a tendency toward N–N bond cleavage and subsequent formation of Tc–nitrido and Tc–imido species. The reactions of

 TABLE 5. Bond lengths (Å) and angles (°) for [Tc–NCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] $\cdot$ 0.25CH<sub>2</sub>Cl<sub>2</sub> (2)

Tc–P(1)	2.464(3)	Tc–Cl(1)	2.377(2)
Tc–N	1.602(8)	Tc–P(1A)	2.462(3)
Tc–Cl(1A)	2.375(2)	P(1)–C(11)	1.820(8)
P(1)–C(21)	1.842(7)	P(1)–C(31)	1.832(6)
C(11)–C(12)	1.377(10)	C(11)–C(16)	1.401(11)
C(12)–C(13)	1.381(13)	C(13)–C(14)	1.373(13)
C(14)–C(15)	1.376(11)	C(15)–C(16)	1.382(11)
C(21)–C(22)	1.390(9)	C(21)–C(26)	1.385(9)
C(22)–C(23)	1.390(11)	C(23)–C(24)	1.388(11)
C(24)–C(25)	1.371(11)	C(25)–C(26)	1.372(10)
C(31)–C(32)	1.395(11)	C(31)–C(36)	1.379(13)
C(32)–C(33)	1.385(9)	C(33)–C(34)	1.363(13)
C(34)–C(35)	1.376(14)	C(35)–C(36)	1.393(11)
P(1)–Tc–Cl(1)	87.8(1)	P(1)–Tc–N	99.1(1)
Cl(1)–Tc–N	109.9(1)	P(1)–Tc–P(1A)	162.0(1)
Cl(1)–Tc–P(1A)	86.1(1)	N–Tc–P(1A)	98.9(1)
P(1)–Tc–Cl(1A)	86.1(1)	Cl(1)–Tc–Cl(1A)	140.3(1)
N–Tc–Cl(1A)	109.8(1)	P(1A)–Tc–Cl(1A)	87.9(1)
Tc–P(1)–C(11)	114.6(2)	Tc–P(1)–C(21)	111.0(3)
C(11)–P(1)–C(21)	106.6(4)	Tc–P(1)–C(31)	116.0(3)
C(11)–P(1)–C(31)	101.4(3)	C(21)–P(1)–C(31)	106.3(3)
P(1)–C(11)–C(12)	117.2(6)	P(1)–C(11)–C(16)	124.6(5)
C(12)–C(11)–C(16)	118.2(7)	C(11)–C(12)–C(13)	121.3(8)
C(12)–C(13)–C(14)	120.3(7)	C(13)–C(14)–C(15)	119.3(8)
C(14)–C(15)–C(16)	120.8(8)	C(11)–C(16)–C(15)	120.1(7)
P(1)–C(21)–C(22)	121.0(5)	P(1)–C(21)–C(26)	119.8(5)
C(22)–C(21)–C(26)	119.1(6)	C(21)–C(22)–C(23)	120.6(6)
C(22)–C(23)–C(24)	119.5(7)	C(23)–C(24)–C(25)	119.3(7)
C(24)–C(25)–C(26)	121.6(7)	C(21)–C(26)–C(25)	119.9(6)
P(1)–C(31)–C(32)	119.7(6)	P(1)–C(31)–C(36)	120.8(6)
C(32)–C(31)–C(36)	119.5(6)	C(31)–C(32)–C(33)	119.6(8)
C(32)–C(33)–C(34)	120.6(8)	C(33)–C(34)–C(35)	120.3(7)
C(34)–C(35)–C(36)	119.9(9)	C(31)–C(36)–C(35)	120.1(8)

[TcOCl<sub>4</sub>]<sup>–</sup> with 1,1-disubstituted organohydrazines yield deep red solutions of a species believed to be [Tc(NNR<sub>2</sub>)Cl<sub>4</sub>]<sup>–</sup> [20, 23]. However, analytically pure compositions of this species cannot be isolated. Thin layer chromatography reveals the presence of three distinct species, and the IR spectrum of this product suggested the presence of both hydrazido species (1550–1600 cm<sup>–1</sup>,  $\nu$ (N=N)) and imido and/or nitrido moieties (1000–1050 cm<sup>–1</sup>,  $\nu$ (Tc=N)). By exploiting the presence of various coligands, discrete Tc–hydrazido(2–) complexes have been isolated. Thus, addition of phosphine ligands or thiolate groups results in crystalline products [TcCl(NNMePh)(dppe)<sub>2</sub>]<sup>+</sup> [23] and [Tc<sub>2</sub>N<sub>2</sub>(NNPh<sub>2</sub>)<sub>2</sub>(SR)<sub>4</sub>] [21]. Likewise, catecholate ligands have been found to stabilize complexes with the highly unusual bridging mode of organohydrazido coordination, reported for [Tc<sub>2</sub>O<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>2</sub>(NNPh<sub>2</sub>)<sub>2</sub>]<sup>–</sup> [44].

The addition of hydralazine–HCl to a solution of [TcOCl<sub>4</sub>]<sup>–</sup> at room temperature, followed by addition of PPh<sub>3</sub>, allowed isolation of the Tc(V)–hydrazido complex [TcCl<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>N<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>] $\cdot$ 0.75C<sub>7</sub>H<sub>8</sub> (1). However, if the reaction is carried out in refluxing CH<sub>2</sub>Cl<sub>2</sub>, N–N bond cleavage appears to be promoted

and the nitrido species  $[\text{TcNCl}_2(\text{PPh}_3)_2]$  (**2**) is the major product.

The IR spectrum of **1** exhibits strong bands at 1482, 1435, 744 and  $693\text{ cm}^{-1}$  consistent with coordinated  $\text{PPh}_3$ . Prominent bands at 1248, 1275, 1354, 1542 and  $1618\text{ cm}^{-1}$  are characteristic of the hydrazino ligand of which the higher energy bands are assigned to  $\nu(\text{N}=\text{N})$ , typically found in the  $1500\text{--}1700\text{ cm}^{-1}$  region for hydrazido(3-) complexes. The bands at 1542 and  $1618\text{ cm}^{-1}$  are of moderate intensity at best reflecting the lower energy stretching frequency of the 'doubly bent' coordination mode and/or the unusual strain in the ligand bite and delocalization of electron density through the metalocycle. No bands attributable to  $\nu(\text{Tc}=\text{O})$  are observed in the  $1000\text{--}700\text{ cm}^{-1}$  region.

The isolation of  $[\text{TcCl}_2(\text{C}_8\text{H}_5\text{N}_4)(\text{PPh}_3)_2]$  demonstrates that the Tc-oxo moiety can react with organohydrazine ligands by the conventional condensation-type reaction. Although oxo-atom abstraction by  $\text{PPh}_3$  is also possible, the IR spectrum of the red-brown material produced prior to addition of  $\text{PPh}_3$  indicates the absence of bands associated with  $\nu(\text{Tc}=\text{O})$  and confirms that  $\text{PPh}_3$  is not the agent responsible for oxo abstraction.

The electronic spectrum of **1** exhibits two intense UV bands at 261 and 330 nm ( $\epsilon = 3.4 \times 10^4$  and  $1.0 \times 10^4\text{ cm}^{-1}\text{ M}^{-1}$ , respectively) and a weak transition in the visible at 574 nm ( $\epsilon = 1.6 \times 10^2\text{ cm}^{-1}\text{ M}^{-1}$ ). The two UV bands are characteristics of structures with the *trans* phosphine coordination, while the band in the visible is tentatively assigned as a d-d transition.

In order to confirm the extent of deprotonation of the hydrazido moiety and the magnetism of complex **1**, the proton NMR spectrum was recorded at room temperature. Only four signals were observed upfield of 15 ppm relative to TMS, all in the 10–7 ppm range, establishing that the ligand is present in the triply deprotonated or hydrazido(3-) form. The six phenyl rings gave rise to two multiplets at 6.9 and 7.4 ppm in the ratio of 3:2. Two signals downfield of these protons at 8.4 (multiplet) and 10.0 (singlet) in the ratio of 4:1 correspond to the five aromatic protons of the phthalazine ring. The integrated ratio of phthalazine protons to phosphine phenyl protons was the anticipated 5:30.

In contrast, the reaction of  $[\text{TcOCl}_4]^-$  with hydrazine  $\cdot\text{HCl}$  in refluxing  $\text{CH}_2\text{Cl}_2$ , followed by addition of  $\text{PPh}_3$  and further refluxing for several hours, yielded the Tc(V)-nitrido species  $[\text{TcNCl}_2(\text{PPh}_3)_2] \cdot 0.25\text{CH}_2\text{Cl}_2$  (**2**) as the major product. Complex **2** was also isolated from reactions of  $[\text{TcOCl}_4]^-$  with disubstituted N,N organohydrazines,  $\text{RR}^1\text{NNH}_2$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5; \text{R}^1 = \text{C}_6\text{H}_5$ ) and from the

reaction of  $[\text{TcCl}_4(\text{PPh}_3)_2]$  with disubstituted organohydrazines. In this latter case, the formation of the Tc(V)-nitrido may be rationalized by the formation of a hydrazido(1-) intermediate, which is subsequently protonated at the more basic  $\beta$ -nitrogen, resulting in N-N bond cleavage and formation of the diorganoamine  $\text{RR}^1\text{NH}$ . Subsequent elimination of HCl and oxidation produces the nitrido species. These observations would suggest that, in the absence of a proton source, the hydrazido species may be isolated. Some evidence for this conclusion is provided by the reaction of  $[\text{TcCl}_4(\text{PPh}_3)_2]$  with disilylated diorganohydrazines  $\text{RR}^1\text{NN}(\text{SiMe}_3)_2$  under analogous conditions. The reaction proceeded smoothly in the presence of oxygen to give  $[\text{TcCl}_3(\text{NNRR}_1)(\text{PPh}_3)_2]$  (**3**). There was no detectable amount of the nitrido complex formed under these conditions.

Complex **2** exhibits strong IR bands at 1078 and  $1085\text{ cm}^{-1}$  which are associated with  $\nu(\text{Tc}=\text{N})$  and  $\text{PPh}_3$  group vibrations. IR absorptions in the  $1050\text{--}1085\text{ cm}^{-1}$  range are characteristic of the Tc(V)-nitrido complexes  $[\text{A}_2\text{Ph}_4][\text{TcNCl}_2(\text{PPh}_3)_2]$  [33],  $[\text{TcBrN}(\text{bipy})_2][\text{BPh}_4]$  and  $[\text{TcBrN}(\text{bipy})_2]_2\text{[TcBr}_4]$  [39]. The band at  $350\text{ cm}^{-1}$  is attributed to  $\nu(\text{Tc}-\text{Cl})$ .

#### Crystal structures of

$[\text{Tc}(\text{C}_8\text{H}_5\text{N}_4)\text{Cl}_2(\text{PPh}_3)_2] \cdot 0.75\text{C}_7\text{H}_8$  and

$[\text{TcNCl}_2(\text{PPh}_3)_2] \cdot 0.25\text{CH}_2\text{Cl}_2$

The structure of **1**, shown in Fig. 1, is isomorphous with that of the analogous rhenium species  $[\text{Re}(\text{C}_8\text{H}_5\text{N}_2)\text{Cl}_2(\text{PPh}_3)_2]$  [24]. The Tc center exhibits distorted octahedral geometry, with the phosphine donors adopting the *trans* axial configuration. The equatorial plane is defined by the two chloride donors

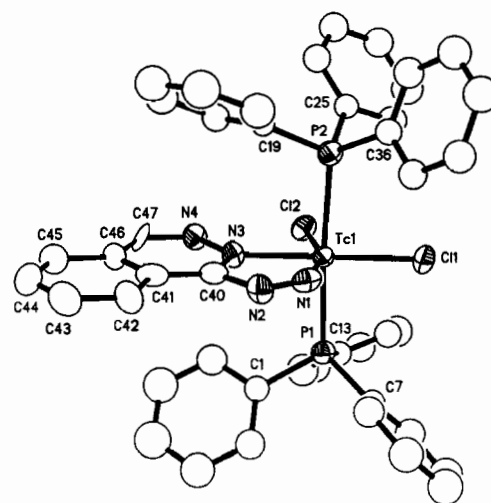


Fig. 1. ORTEP view of  $[\text{Tc}(\text{C}_8\text{H}_5\text{N}_4)\text{Cl}_2(\text{PPh}_3)_2]$ , showing the atom-labelling scheme.

and the nitrogen donors of the chelating hydralazino ligand.

The Tc–P and Tc–Cl average bond lengths, 2.484(6) and 2.379(5) Å, respectively, are within the range observed for Tc–P and Tc–Cl bond lengths for Tc(III), Tc(IV) and Tc(V) complexes [45–47], suggesting that these distances are relatively insensitive to the formal oxidation state of the metal. The Tc–Cl(1) bond *trans* to the phthalazine N donor is significantly longer than the Tc–Cl(2) bond which is *trans* to the hydrazido nitrogen. As indicated by the metrical parameters given in Table 3, there is considerable delocalization throughout the Tc–N(1)–N(2) unit. The short Tc–N(1) distance of 1.77(1) Å is consistent with significant multiple bonding, in contrast to the Tc–N(3) distance of 2.151(9) Å which approaches the calculated limit for a Tc–N(sp<sup>2</sup>) single bond. Similarly the N(1)–N(2) distance of 1.27(2) Å is significantly shorter than the N(3)–N(4) distance of 1.38(1) Å, suggesting a bond order approaching 2 for N(1)–N(2). As illustrated in Table 6, the geometry of the Tc–N(1)–N(2) moiety may be compared to those observed for [Tc(NNC<sub>6</sub>H<sub>4</sub>Br)<sub>2</sub>Cl(PPh<sub>3</sub>)<sub>2</sub>] [17] and [Tc<sub>2</sub>N<sub>2</sub>(NNPh<sub>2</sub>)<sub>2</sub>(SC<sub>6</sub>H<sub>2</sub>Pr<sub>3</sub>)<sub>4</sub>] [21] and contrasted to that of [TcO(SC<sub>6</sub>H<sub>2</sub>Pr<sub>3</sub>)(PhNNCON<sub>2</sub>HPh)] [18] where  $\pi$ -bonding to the oxo group and the requirements of sp<sup>2</sup> hybridization at N(1) preclude significant Tc–N multiple bond interactions.

The most significant structural features of **1** are found in the hydrazidophthalazine ligand. The metrical parameters of the ligand suggest charge delocalization over the entire phthalazino–metallocycle ring system. As noted above, the N1–N2 bond distance of 1.274(17) Å is consistent with double bond character. The bicyclic aromatic phthalazine ring appears structurally unperturbed with an average bond distance of 1.39(3) Å. The N2–C40 bond distance of 1.403(15) Å suggests a bond order of 1.5 and delocalization of electron density throughout the entire ligand. The average bond angle of the phthalazine ring system of 120(3)° suggests that the ligand strain is localized in the Tc–N1–N2–C40–N3 ring. As further evidence for delocalization of the electron density throughout the phthalazino–metallocycle ring system the Tc–N1–N2–C40 unit is planar within a deviation

of 0.0002 Å and the entire Tc–hydralazino unit is planar within a deviation of 0.018 Å.

The requirements of chelate ring formation constrain the N(3)–Tc–N(1) ligand bite angle to 69.8(4)° and the Tc–N(1)–N(2) angle to 138.6(7)°. The bidentate coordination of the hydralazine ligand forces the hydrazine function to mimic the ‘doubly bent’ coordination mode of the monodentate hydrazido(3–) ligands where the M–N–N and N–N–R angles approach 115 and 135°, respectively, rather than the ‘singly bent’ coordination mode where angles of 170–180° and 118–125°, respectively, are observed.

The molecular geometry and atom numbering of complex **2** are shown in Fig. 2. Interatomic bond distances and angles are given in Table 5. The coordination geometry about technetium is best described as distorted square pyramidal with the nitrido nitrogen atom at the apical position, and P(1), Cl(1), Cl(1a) and P(1a) defining the equatorial plane. The technetium atom sits 0.59 Å above the P(1)–Cl(1)–Cl(1a)–P(1a) plane displaced towards the apical nitrogen. An analysis [48] of the molecular geometry gives a  $\tau$  value of 0.37 which falls within the structural continuum of trigonal bipyramidal and rectangular pyramidal geometries.

The Tc–N distance of 1.602(8) Å is comparable to that reported for other examples of Tc–nitrido species, listed in Table 7. The Tc–N bond distances listed reflect both the coordination numbers and the presence of bulky and/or other  $\pi$ -bonding ligands. Thus, five coordinate species with ligands which are relatively non-demanding sterically fall in the 1.58–1.61 Å range, while six coordinate species fall in the 1.61–1.63 Å range. The presence of both  $\pi$ -bonding coligands and bulky thiolate donors is reflected in the 1.64 Å Tc–N distance of [Tc<sub>2</sub>N<sub>2</sub>(NNPh<sub>2</sub>)<sub>2</sub>(SC<sub>6</sub>H<sub>2</sub>Pr<sub>3</sub>)<sub>4</sub>] [21]. Although this trend in Tc–N distances is unexceptional, it should be noted that the errors associated with the Tc–N distances in many of these structures are in the order of 0.01 Å, making detailed correlations tenuous at best.

TABLE 6. Comparison of Tc–N–N fragments for Tc–hydrazido and related functional units<sup>a</sup>

Complex	Tc–N	N–N	Tc–N–N
[Tc(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> )Cl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	1.77(1)	1.27(2)	138.6(7)
[Tc(NNC <sub>6</sub> H <sub>4</sub> Br) <sub>2</sub> Cl(PPh <sub>3</sub> ) <sub>2</sub> ]	1.790(11)	1.227(12)	169.0(9)
[TcO(SC <sub>6</sub> H <sub>2</sub> Pr <sub>3</sub> ) <sub>2</sub> (PhNNCON <sub>2</sub> HPh)]	2.139(2)	1.298(3)	117.5(2)
[Tc <sub>2</sub> N <sub>2</sub> (NNPh <sub>2</sub> ) <sub>2</sub> (SC <sub>6</sub> H <sub>2</sub> Pr <sub>3</sub> ) <sub>4</sub> ]	1.88(1)	1.25(2)	140.0(12)

<sup>a</sup>Bond lengths in Å; bond angles in °.

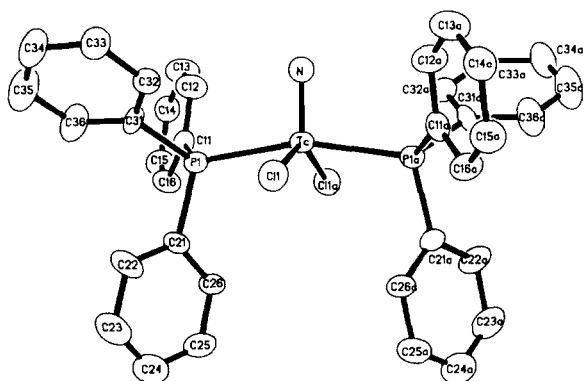


Fig. 2. ORTEP view of  $[\text{TcNCl}_2(\text{PPh}_3)_2]$ .

TABLE 7. Comparison of Tc-N(nitrido) distances for five and six coordinate technetium complexes

Complex	Tc-N	Reference
$[\text{TcNCl}_2(\text{PPh}_3)_2]$	1.602(8)	this work
$[\text{AsPh}_4][\text{TcNCl}_4]$	1.581(5)	31
$[\text{TcN}(\text{S}_2\text{CNEt}_2)_2]$	1.604(6)	32
$[\text{TcN}(\text{C}_9\text{H}_6\text{NS})_2]$	1.623(4)	33
$[\text{TcN}(\text{NCS})_2(\text{CH}_3\text{CN})(\text{PPh}_3)_2]$	1.629(4)	34
$[\text{AsPh}_4][\text{Tc}_4\text{N}_4\text{O}_2(\text{oxalate})_6]$	1.622(17) av.	35
$[\text{AsPh}_4][\text{TcNBr}_4]$	1.596(6)	36
$[\text{TcN}(\text{C}_9\text{H}_6\text{N}_2\text{S}_2)(\text{PPh}_3)]$	1.611(3)	37
$[\text{TcN}(\text{C}_9\text{H}_6\text{N}_2\text{S}_2)_2]$	1.612(3)	37
$[\text{TcNBr}(\text{bipy})_2][\text{TcBr}_4]$	1.609(20)	38
$[\text{A}_2\text{Ph}_4][\text{TcN}(\text{S}_2\text{C}_2\text{O}_2)_2]$	1.606(7)	30
$[\text{TcN}(\text{SC}_6\text{HMe}_4)_2[\text{NHC}(\text{NMe}_2)_2]$	1.615(6)	29
$[\text{Tc}_2\text{N}_2(\text{NNPh})_2(\text{SC}_6\text{H}_2\text{Pr}_3)_4]$	1.64(1)	21

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