Nitrido- and Oxo-technetium(v) Chelate Complexes with N_2S_2 Ligands: Synthesis and Crystal Structures†

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Diaminedithiol ligands (N_2S_2) of the type $HSCR_2CH_2NR'CH_2CH_2NR'CH_2CR_2SH$, where R = Me or Et and R' = Me or Et (H_2L) or H (H_4L), react with $[TcNCl_2(PPh_3)_2]$ and $[AsPh_4][TcOCl_4]$ forming neutral or cationic complexes of technetium(v) containing the $[Tc{\equiv}N]^{2+}$ and $[Tc{=}O]^{3+}$ moieties, respectively. They are stable in the range pH 2–12.5; at pH 12.5 the oxo-complexes with H_4L become neutral due to deprotonation of one of two NH groups. The complexes have been characterized by elemental analysis, IR and ^1H NMR spectra, magnetic susceptibility and conductivity measurements. The structures of $[TcO(L^1)][BPh_4]$ (R = Me, R' = Et) and $[TcO(H_2L^3)]Cl$ (R = Et, R' = H) have been determined by single-crystal X-ray analysis. The co-ordination around Tc^V is distorted square-pyramidal in each case where the Tc atom is displaced from the plane defined by N(1), N(2), S(1), S(2) towards the O atom by 0.774(1) and 0.7731(3) Å, respectively.

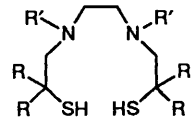
Intensive studies of the chemistry of the long-lived radionuclide ^{99}Tc, a β-emitter ($t_{\frac{1}{2}} = 2.1 \times 10^5$ y) available in macroscopic quantities, have been made due to the importance of the metastable isomer ^{99m}Tc in the practice of nuclear medicine. The choice of this radioisotope for imaging in diagnostic nuclear medicine stems from its ideal photon energy of 140 KeV, half-life of 6 h and convenient availability.

Several technetium complexes with chelating agents containing O, S, N and P donor atoms have been prepared, but only neutral, lipophilic complexes of ^{99m}Tc are able to cross the blood–brain barrier. Recently, the development of N_2S_2 chelating ligands has led to neutral and lipophilic complexes which cross the intact brain–barrier.[1–4]

Davison and co-workers[5,6] prepared and characterized a class of oxotechnetium(v) complexes with a series of tetradentate diamidedithiol ligands. The complex $[TcO(ema)]^-$ [H_4ema = *N*,*N'*-ethylenebis(2-mercaptoacetamide)] in which the amide and thiolate groups are deprotonated showed renal clearance in animals and in humans.[7–9] The H_4ema ligand was modified by Davison to give trianionic derivatives which led to five-co-ordinated oxotechnetium(v) complexes.[10] The oxo-technetium(v) complexes containing diamidedithiol ligands[5,6] were characterized by elemental analysis, conductivity, IR, UV, ^1H and ^{13}C NMR spectroscopy, and one complex was structurally characterized.[10] Subsequently, a series of diaminedithiol complexes were structurally characterized.[11]

It is expected that the nature of this kind of ligand would lead to *syn* and *anti* configurations of *N*-alkyl groups as well as of substituents on the carbon back-bone with respect to the $[TcO]^{3+}$ or $[TcN]^{2+}$ core.[11] Fritzberg and co-workers[12] isolated the two *syn* and *anti* epimers of technetium and one of rhenium of general formula $[XPh_4][MO(map)]$ [X = As or P; M = Tc or Re; map = 2,3-bis(mercaptoacetamido)propanoate], and their crystal structures were determined. Moreover, studies carried out on animals and humans showed that the *syn* complex of Tc is excreted faster than the *anti* by the kidney receptors.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



H_2L^1 R' = Et, R = Me
H_2L^2 R' = R = Me
H_4L^3 R' = H, R = Et
H_4L^4 R' = H, R = Me

To date, three types of ligands are employed as agents for brain perfusion imaging: propyleneamine oxime, diaminedithiol or bis(aminoethanethiol) and ethyl cysteinate dimer. 3,6,6,9-Tetramethyl-4,8-diazaundecane-2,10-dione dioxime forms a lipophilic and neutral complex with ^{99m}Tc giving high brain uptake and good retention;[13] the diaminedithiol or bis(aminoethanethiol) analogues possess the same N_2S_2 backbone, giving lipid-soluble complexes of ^{99m}Tc which show a high initial brain uptake.[14] Recently, N_2S_2 ligands containing ester functions have been synthesised[15] and the corresponding complexes with ^{99m}Tc seem to be useful as cerebral blood-flow imaging agents.[16] With such ligands, deprotonation of the NH and SH groups and the charge of the central metal core will determine the final net charge of the complex, while its lipophilicity can be adjusted in a convenient manner by using different substituents on the ligand.

In the present study a series of tetradentate symmetrical diaminedithiols was employed to investigate the synthesis and stability of nitrido- and oxo-technetium(v) complexes obtained by substitution reactions of $[TcNCl_2(PPh_3)_2]$ and $[TcOCl_4]^-$. The crystal structues of $[TcO(L^1)]^+$ and $[TcO(H_2L^3)]^+$ have also been determined. A preliminary study on the biodistribution of $[^{99m}TcN(L)]$ complexes is described.

Results and Discussion

Neutral nitrido-complexes $[TcN(L^n)]$ (n = 1 or 2) and $[TcN(H_2L^n)]$ (n = 3 or 4) are easily prepared from the starting square-pyramidal $[Tc^VNCl_2(PPh_3)_2]$ complex by simple substitution reactions. The formulation of the complexes is supported by elemental analysis, conductivity and magnetic susceptibility measurements, IR and ^1H NMR spectra. Conductivity values ranged from 2.5×10^{-4} to 7×10^{-4} S cm^2 mol^{-1} in MeCN at 20 °C, indicative of the neutral character of

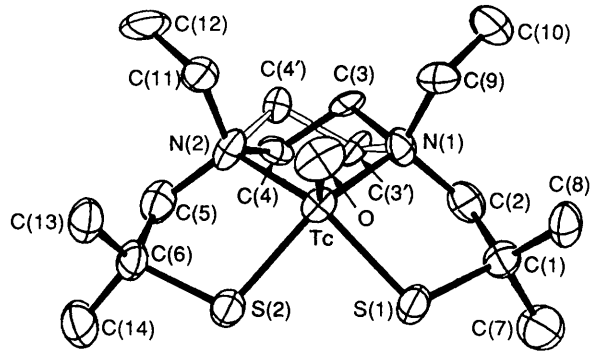


Fig. 1 An ORTEP[22] view of the cation of compound **1a** displaying the thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity

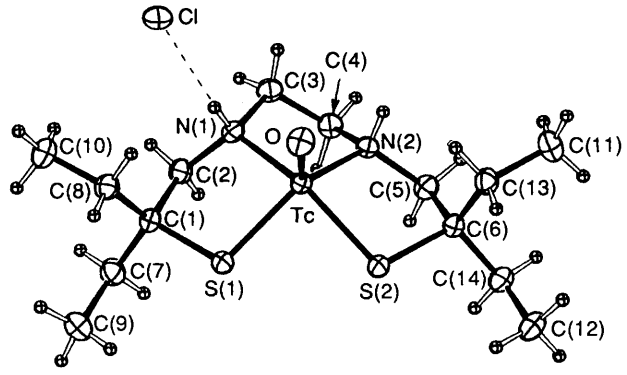


Fig. 2 An ORTEP[22] view of the asymmetric unit of compound **1c** displaying the thermal ellipsoids at 30% probability

the complexes [TcN(L^n)] (n = 1 or 2). Magnetic susceptibility data reveal that they are diamagnetic, in accord with a d^2 closed-shell configuration characteristic of a $[Tc{\equiv}N]^{2+}$ core.[17] The complexes [TcN(H_2L^n)] (n = 3 or 4) are insoluble in common organic solvents, but soluble in hot dimethylformamide. All these complexes are pale yellow air-stable solids. Their infrared spectra showed the absorption of the Tc≡N group in the range 1060–1070 cm^{-1}, comparable with values reported for other technetium nitrido complexes;[18] the N–H absorption occurred in the range 3000–3150 cm^{-1} for the [TcN(H_2L^n)] (n = 3 or 4) complexes.

Reaction of the H_2L and H_4L ligands with [$AsPh_4$]-[$TcOCl_4$] gave complexes formulated as $[TcO(L^n)]^+$ (n = 1 or 2) and $[TcO(H_2L^n)]^+$ (n = 3 or 4) and if no counter ion was added the corresponding chloride salts were obtained. These complexes are orange and air-stable solids, soluble in polar organic solvents. They have been characterized by elemental analysis, IR and ^1H NMR spectroscopy and conductivity measurements. Conductivity data showed that they carried a positive charge. The absorption of the Tc=O group in the range 950–960 cm^{-1} is comparable with values reported for other oxotechnetium(v) complexes containing N_2S_2 ligands.[5,6,10–12] Furthermore, infrared spectra for $[TcO(H_2L^n)]^+$ (n = 3 or 4) complexes showed characteristic N–H · · · Cl bond stretching in the range 2500–2700 cm^{-1}.[11b]

Under alkaline conditions (pH 12.5) the $[TcO(H_2L^n)]^+$ complexes seem to undergo deprotonation, ν(Tc=O) being found at 890 cm^{-1} and ν(NH) at 3150 cm^{-1}. Conductivity measurements suggested a neutral species was formed, probably [TcO(HL^n)]. The accepted range[10] for the Tc=O stretch is 860–970 cm^{-1} in five-co-ordinate oxotechnetium(v) complexes and the lower stretching frequency observed for these complexes indicates a weakening of the metal–oxo bond due to the greater charge of the dithiolate ligand.

The ligands H_2L and H_4L, which are polydentate and polyprotonic, reveal their versatility in that they can form very stable, neutral five-co-ordinate nitridotechnetium(v) complexes as well as oxotechnetium cations. In addition, the H_4L ligands produce neutral oxotechnetium(v) compounds depending on pH of the reaction mixture. Diaminedithiol ligands span the basal position of square-pyramidal nitrido technetium(v) complexes. It is well known that the chemistry of the $[TcN]^{2+}$ core is characterized by the formation of five-co-ordinate complexes with Schiff bases, dithiocarbamate and dithiocarbazate ligands,[18a,19f,20a,b,21] while only recently octahedral complexes have been reported.[18b,c] In the present complexes we expected the formation of two isomers because the *N*-alkyl groups of the ligands can assume a *syn* or *anti* configuration with respect to the Tc≡N core, as previously observed with other N_2S_2 ligands.[11]

Table 1 Fractional coordinates for compound **1a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Tc	0.427 78(5)	0.649 54(5)	0.539 60(4)
S(1)	0.417 1(2)	0.779 7(1)	0.474 0(2)
S(2)	0.512 4(2)	0.606 0(2)	0.434 9(2)
O	0.496 3(4)	0.663 6(5)	0.615 7(4)
N(1)	0.283 4(5)	0.673 8(4)	0.568 7(4)
N(2)	0.375 4(5)	0.512 8(4)	0.534 7(5)
C(1)	0.304 0(7)	0.827 4(6)	0.506 2(5)
C(2)	0.239 8(6)	0.748 5(7)	0.521 2(6)
C(3)[a]	0.233 7(9)	0.582 4(8)	0.569 7(8)
C(4)[a]	0.273 3(10)	0.527 6(9)	0.508 1(7)
C(3')[b]	0.229 3(15)	0.603 2(12)	0.524 8(12)
C(4')[b]	0.267 7(13)	0.514 8(12)	0.553 2(12)
C(5)	0.412 1(7)	0.459 1(6)	0.466 9(6)
C(6)	0.510 4(6)	0.483 0(6)	0.441 2(6)
C(7)	0.264 7(8)	0.877 0(9)	0.435 8(7)
C(8)	0.317 4(7)	0.892 0(6)	0.573 4(6)
C(9)	0.277 8(9)	0.695 3(7)	0.652 4(5)
C(10)	0.183 3(11)	0.706 5(10)	0.686 9(7)
C(11)	0.398 7(7)	0.467 7(7)	0.609 0(6)
C(12)	0.361 6(14)	0.376 1(8)	0.619 9(7)
C(13)	0.584 9(7)	0.448 9(6)	0.495 7(6)
C(14)	0.526 1(9)	0.445 3(8)	0.360 9(6)

[a] Occupancy = 0.6. [b] Occupancy = 0.4.

Proton NMR Spectra.—The ^1H NMR spectra of the soluble nitrido-complexes [TcN(L^n)] (n = 1 or 2) showed resonances characteristic of the Tc(N_2S_2) chelates. In the case of [TcN(L^1)] two complex multiplets of equal intensity were observed at δ 2.85–3.15 and assigned to CH_2 of the AB system of NCH_2CH_3, while the CH_3 group was assigned at δ 1.6, the methyl groups of $SC(Me)_2$ as two signals at δ 1.7–3.35, and the remaining protons ($CH_2NCH_2CH_2NCH_2$) were attributed to a set of resonances at δ 2.6–2.8. The spectrum of [TcN(L^2)] is more difficult to interpret. It showed a set of two complex multiplets at δ 3.7–4.2 of equal intensity, attributable to the NCH_2 system, another set at δ 2.65–3.10 assigned to the NMe group, and two doublets at δ 2.3 and 3.2 which might be assigned to the CMe_2 group.

These data suggested, in the absence of crystal structures, a *syn* configuration for the first complex, and taking into account the complexity of the ^1H NMR spectrum, an *anti* configuration for [TcN(L^2)]. On the other hand, TcN(N_2S_2) nitrido complexes have not been characterized up to now, and all attempts to obtain suitable crystals for X-ray investigations have failed.

The ^1H NMR spectra of complexes $[TcO(L^n)]^+$ (n = 1 **1a** or 2 **1b**) showed a *syn* and *anti* configuration respectively according to literature data.[5,6,10,11] For **1a** a set of two multiplets at δ 4.2 and 4.5 and a triplet at δ 1.5 were assigned to the NCH_2CH_3 system, and two singlets at δ 1.7 and 1.9 were assigned to the CMe_2 group. For complex **1b** the two CMe_2 groups exhibited four resonances at δ 1.65–2.05, while two singlets at δ 2.46 and 3.70 were attributed to the NMe groups.

Table 2 Fractional coordinates for compound **1c** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Tc	0.005 09(1)	0.245 61(1)	0.562 28(1)
Cl	0.216 59(5)	0.518 15(4)	0.529 95(6)
S(1)	0.139 05(4)	0.142 55(4)	0.638 41(4)
S(2)	−0.106 65(4)	0.104 53(3)	0.562 92(4)
O	0.022 5(1)	0.277 6(1)	0.435 5(1)
N(1)	0.089 7(1)	0.361 3(1)	0.658 0(1)
N(2)	−0.129 2(1)	0.317 7(1)	0.628 9(1)
C(1)	0.240 3(2)	0.234 6(1)	0.705 3(2)
C(2)	0.171 1(2)	0.323 3(1)	0.744 9(1)
C(3)	0.010 3(2)	0.439 4(1)	0.696 3(2)
C(4)	−0.090 9(2)	0.383 2(1)	0.724 7(2)
C(5)	−0.224 9(2)	0.252 2(1)	0.651 1(2)
C(6)	−0.243 9(1)	0.165 8(1)	0.568 6(1)
C(7)	0.320 5(2)	0.270 1(2)	0.623 7(2)
C(8)	0.297 1(2)	0.178 8(2)	0.804 6(2)
C(9)	0.411 3(2)	0.342 6(2)	0.668 9(2)
C(10)	0.370 3(2)	0.088 1(2)	0.780 9(2)
C(11)	−0.347 5(2)	−0.008 7(2)	0.542 9(2)
C(12)	−0.397 5(2)	0.254 7(2)	0.444 0(3)
C(13)	−0.322 4(2)	0.086 3(2)	0.613 8(2)
C(14)	−0.283 7(2)	0.204 7(2)	0.455 4(2)
H(N1)	0.124(2)	0.392(1)	0.613(1)
H(N2)	−0.152(2)	0.361(2)	0.577(2)

In order to confirm our assignment a crystal structure determination of **1a** was undertaken (see below). The complex $[TcO(H_2L^3)]^+$ **1c** showed a series of multiplets hardly interpretable, and the assignment of a *syn* configuration was made from the X-ray crystal structure (see below). The complex $[TcO(H_2L^4)]^+$ **1d** showed a set of singlets at δ 1.60–2.0 and we assign it an *anti* configuration as for **1b**. Finally, the ^1H NMR spectra of $[TcO(HL^n)]$ (n = 3 **1e** or 4 **1f**) comprised a series of complex multiplets somewhat difficult to interpret.

It is interesting that both nitrido- and oxo-complexes containing the H_2L^1 ligand possess a *syn* configuration, while the corresponding L^2 compounds show an *anti* one. This fact cannot be due to steric impediments but rather to the strength and distortion of ligands which when co-ordinated to a central metal do not allow fluxionality. On the other hand, Davison and co-workers[10] demonstrated the presence of only one isomer with a high energy barrier to inversion.

The Structures of Complexes **1a** *and* **1c**.—The crystal structure of complex **1a** consists of square-pyramidal $[Tc^VO(L^1)]^+$ cations and $[BPh_4]^-$ anions, packed together by means of van der Waals interactions. The co-ordination around Tc^V is distorted square-pyramidal, with the oxygen at the apical position and the N(1), N(2), S(1), S(2) atoms of the L^1 ligand forming the basal plane (Fig. 1).[22] The Tc atom is displaced from the mean plane defined by N(1), N(2), S(1), S(2) towards the O atom by 0.774(1) Å, and the straight line connecting Tc to the O atom makes an angle of 0.92(3)° with the normal to the mean plane.

The conformations of the five-membered rings formed by the ligands and Tc, [R1: Tc, S(1), C(1), C(2), N(1). R2: Tc, S(2), C(6), C(5), N(2). R3: Tc, N(1), C(3), C(4), N(2). R3′: Tc, N(1), C(3′), C(4′), N(2)], described using puckering parameters,[23] are reported in Table 4. Rings R3 and R3′ concern the disordered part of the molecule and they adopt opposite mixed twisted-envelope conformations, *i.e.* $^4T_5/^4E$ (R3) and $^3T_2/^3E$ (R3′).

The asymmetric unit of complex **1c** consists of a square-pyramidal $[Tc^VO(H_2L^3)]^+$ cation and a Cl^- anion (Fig. 2). The spatial arrangement of the atoms around the Tc is similar to that found in complex **1a**. The Tc atom is displaced from the mean plane defined by N(1), N(2), S(1), S(2) towards the O atom by 0.7731(3) Å, and the straight line connecting Tc to the O atom makes an angle of 2.66(5)° with the normal to the mean plane. The conformation of five-membered rings R1, R2 and R3 are reported in Table 4. The molecular packing is mainly controlled by N–H ··· Cl hydrogen bonds, where the Cl anions bridge two complex cations: N(1)–H(1) 0.83(2), N(1) ··· Cl 3.068(1), H(N1) ··· Cl 2.28(2) Å, N(1)–H(N1) ··· Cl 161(1)°; and N(2)–H(N2) 0.88(2), N(2) ··· Cl 3.027(1), H(N2) ··· Cl 2.15(2) Å, N(2)–H(N2) ··· Cl 171(2)° ($-x$, $1-y$, $1-z$).

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

	Compound **1a**	Compound **1c**
Tc–S(1)	2.253(2)	2.2494(6)
Tc–S(2)	2.265(3)	2.2731(6)
Tc–O	1.648(6)	1.657(1)
Tc–N(1)	2.154(7)	2.121(1)
Tc–N(2)	2.177(6)	2.107(1)
S(1)–C(1)	1.851(10)	1.857(2)
S(2)–C(6)	1.840(10)	1.853(1)
N(1)–C(2)	1.517(12)	1.485(2)
N(1)–C(3)	1.539(14)	1.500(2)
N(1)–C(3′)	1.513(21)	
N(2)–C(4)	1.549(16)	1.501(2)
N(2)–C(4′)	1.567(16)	
N(2)–C(5)	1.509(13)	1.482(2)
C(1)–C(2)	1.516(14)	1.526(3)
C(3)–C(4)	1.452(18)	1.495(3)
C(3′)–C(4′)	1.507(23)	
C(5)–C(6)	1.516(13)	1.519(2)
S(1)–Tc–S(2)	83.4(1)	86.32(2)
S(1)–Tc–O	109.2(3)	113.66(5)
S(1)–Tc–N(1)	84.6(2)	83.19(4)
S(1)–Tc–N(2)	140.1(2)	130.84(4)
S(2)–Tc–O	110.5(2)	109.06(5)
S(2)–Tc–N(1)	138.1(2)	145.58(4)
S(2)–Tc–N(2)	83.3(2)	82.56(4)
O–Tc–N(1)	111.3(3)	105.18(6)
O–Tc–N(2)	110.8(3)	115.24(6)
N(1)–Tc–N(2)	80.6(2)	79.87(5)
Tc–S(1)–C(1)	104.0(3)	103.80(5)
Tc–S(2)–C(6)	103.4(3)	101.40(5)
Tc–N(1)–C(2)	113.1(5)	115.9(5)
Tc–N(1)–C(3)	107.2(6)	110.9(1)
Tc–N(1)–C(3′)	105.0(7)	
C(2)–N(1)–C(3)	118.0(7)	113.5(1)
C(2)–N(1)–C(3′)	92.0(9)	
Tc–N(2)–C(4)	101.7(6)	111.1(1)
Tc–N(2)–C(4′)	108.0(6)	
Tc–N(2)–C(5)	114.1(5)	117.8(1)
C(4)–N(2)–C(5)	100.1(7)	111.8(2)
C(4′)–N(2)–C(5)	120.4(8)	
S(1)–C(1)–C(2)	103.6(3)	105.2(1)
N(1)–C(2)–C(1)	114.5(7)	111.5(1)
N(1)–C(3)–C(4)	108.3(10)	108.2(1)
N(2)–C(4)–C(3)	103.3(10)	107.1(2)
N(1)–C(3′)–C(4′)	105.1(13)	
N(2)–C(4′)–C(3′)	108.4(11)	
N(2)–C(5)–C(6)	115.0(7)	111.8(2)
S(2)–C(6)–C(5)	105.5(6)	104.6(1)

The Tc=O bond distances of 1.648(6) Å in complex **1a** and 1.657(1) Å in **1c** indicating strong multiple-bond character are in perfect agreement with those found in other square-pyramidal technetium(v) complexes.[10–12,24,25] The Tc–S bond distances of 2.253(2) and 2.265(3) Å in **1a** and 2.2494(6) and 2.2731(6) Å in **1c** are within the range 2.24–2.29 Å for typical technetium(v) oxothiolate complexes.[10,12,24,26]

The most interesting feature of these compounds is the difference in the values of the Tc–N(amine) bond distances. In **1a** the values [2.154(7) and 2.177(6) Å] fall in the range 2.15–2.22 Å found in oxo- or nitrido-technetium(v) derivatives where the N(amine) atoms are not involved in hydrogen bonds.[18b,c26] On the other hand, in **1c** the values of 2.121(1) and 2.107(1) Å

Table 4 Puckering coordinates describing the conformations of the rings formed by the bonded ligands L^1 and L^3, with e.s.d.s in parentheses

Ring conformation	Compound	φ/°	Q/Å	
R1 [Tc, S(1), C(1), C(2), N(1)]	**1a**	−94.1(8)	0.410(9)	$^4T_3$
	1c	±87.1(1)	0.443(2)	$^3T_4$ (or $^4T_3$)*
R2 [Tc, S(2), C(6), C(5), N(2)]	**1a**	68.8(9)	0.450(8)	^3E
	1c	±93.6(2)	0.441(2)	$^3T_4$ (or $^4T_3$)*
R3 [Tc, N(1), C(3), C(4), N(2)]	**1a**	−66.2(9)	0.59(1)	$^4T_5/^4E$
	1c	±112.7(2)	0.494(2)	E_3 (or E_4)*
R3′ [Tc, N(1), C(3′), C(4′), N(2)]	**1a**	64(1)	0.55(1)	$^3T_2/^3E$

* Because of the centrosymmetry both enantiomers are present in the crystal.

are indicative of a partial negative charge on the nitrogens as a consequence of a strong polarization of the N–H bonds due to the N–H · · · Cl hydrogen bonds. Such an effect has been observed in similar structures where N–H groups are involved in hydrogen bonds with chloride anions or water molecules,[11b,18c,27] the observed Tc–N range being 2.11–2.14 Å. In order to stress the effect of the partial negative charge on the nitrogens it is noteworthy that the values reported above lie in between Tc–N(amine) distances where the amine groups are not involved in hydrogen bonds and Tc–N(amide) distances 1.96–2.05 Å) where the nitrogen atoms are deprotonated and the negative charges are delocalized on the amide fragments.[10,11c,12,18c,27]

Radiopharmaceutical Preparations.—The nitrido complexes of ^{99m}Tc were prepared according to our procedure,[28] but the exchange reactions were carried out at 40 °C for 15 min. Chromatographic analysis showed the formation of only one product in each case, the yield being 95% for H_2L and 90% for H_4L. The compounds could be formulated as $[TcN(L^n)]$ (n = 1 or 2) and $[TcN(HL^n)]^-$ (n = 3 or 4). A high hepatic fixation and a low renal clearance of the [TcN(L)] compounds demonstrated a higher lipophilicity than the complexes obtained with H_4L ligands which underwent a rapid renal excretion indicative of their anionic character.[6]

Experimental

Materials.—Technetium-99 emits a low-energy (0.292 keV, *ca.* 4.67×10^{-17} J) β^- particle with a half-life of 2.12×10^5 y. All manipulations of solids and solutions were performed in a laboratory approved for the handling of radioisotopes. Normal radiation safety procedures must be used to prevent contamination and bremsstrahlung is not a significant problem due to the low energy of the β-particle emission.

All common laboratory chemicals were of reagent grade and used without purification. Technetium, as aqueous $NH_4[^{99}TcO_4]$ in 0.1 mol dm^{-3} ammonia solution, was purchased from the Radiochemical Centre, Amersham. The compounds $[AsPh_4][TcOCl_4]$, $[TcCl_4(PPh_3)_2]$, $[AsPh_4][TcNCl_4]$ and $[TcNCl_2(PPh_3)_2]$ were prepared by literature methods,[19] as were the ligands H_2L^1 = 4,7-diethyl-2,9-dimethyl-4,7-diazadecane-2,9-dithiol, H_2L^2 = 2,4,7,9-tetramethyl-4,7-diazadecane-2,9-dithiol, H_4L^3 = 3,10-diethyl-5,8-diazadodecane-3,10-dithiol and H_4L^4 = 2,9-dimethyl-4,7-diazadecane-2,9-dithiol.[11a]

Infrared spectra were recorded on a Perkin-Elmer 599 grating spectrometer using KBr pellets, proton NMR spectra of CD_3NO_2 and $CDCl_3$ solutions on a Varian Gemini 300 spectrometer with $SiMe_4$ as internal standard. Elemental analyses were performed on a model 1106 Carlo Erba elemental analyzer. Radioactive technetium was determined after dissolution of the samples in nitric acid–hydrogen peroxide solutions on a model TRICARB 300 C Packard liquid scintillation instrument with Imstagel as scintillator. Conductivity measurements were performed in $MeNO_2$ or MeCN solutions with an Amel model 134 conductivity meter at 20 °C.

Synthesis of the Nitrido Complexes $[TcN(L^n)]$ (n = 1 *or* 2) *and* $[TcN(H_2L^n)]$ (n = 3 *or* 4).—All of the complexes were prepared by the same general procedure.

A sample of $[TcNCl_2(PPh_3)_2]$ (0.2 g, 0.28 mmol) was dissolved in CH_2Cl_2–EtOH (3:1, 40 cm^3) and the resulting pink solution was heated to 40 °C. The dihydrochloride salt of the appropriate ligand in stoichiometric ratio (1:1) was dissolved in water (1 cm^3) and 1 mol dm^{-3} aqueous NaOH was added until pH 9. Then the free ligand was extracted by CH_2Cl_2 and added dropwise to the hot solution of the starting technetium complex. After a few minutes the colour became pale yellow and heating was ceased after 20 min. Pale yellow crystals of the final product were obtained by slow evaporation of the solvent in air. Yield ≥90% for all the complexes. Recrystallization was from CH_2Cl_2–EtOH for $[TcN(L^n)]$ and from hot dimethylformamide for $[TcN(H_2L^n)]$. The complexes are indefinitely stable in air. Λ(MeCN) 1.5×10^{-4}–7×10^{-4} S cm^2 mol^{-1} at 20 °C.

$[TcN(L^1)]$ (Found: C, 41.80; H, 7.50; N, 10.25; S, 14.85; Tc, 23.60. $C_{14}H_{30}N_3S_2Tc$ requires C, 41.65; H, 7.50; N, 10.40; S, 15.90; Tc, 24.55%); ν(Tc≡N) 1060 cm^{-1} (KBr). $\delta_H(CDCl_3)$ 2.85–3.15 (4 H, m, CH_2CH_3), 1.6 (6 H, s, CH_2CH_3), 1.7–3.35 (12 H, s, CMe_2) and 2.6–2.8 (8 H, d, CH_2NCH_2).

$[TcN(L^2)]$ (Found: C, 38.40; H, 6.70; N, 10.90; S, 16.30; Tc, 25.50. $C_{12}H_{26}N_3S_2Tc$ requires C, 38.40; H, 7.00; N, 11.20; S, 17.00; Tc, 26.40%); ν(Tc≡N) 1070 cm^{-1} (KBr). $\delta_H(CDCl_3)$ 3.7–4.2 (8 H, m, CH_2NCH_2), 2.65–3.10 (6 H, m, NMe) and 2.3–3.2 (12 H, d, CMe_2).

$[TcN(H_2L^3)]$ (Found: C, 41.70; H, 7.55; N, 10.30; S, 14.70; Tc, 22.80. $C_{14}H_{30}N_3S_2Tc$ requires C, 41.65; H, 7.50; N, 10.40; S, 15.90; Tc, 24.55%); ν(Tc≡N) 1060 and ν(NH) 3000–3150 cm^{-1} (KBr).

$[TcN(H_2L^4)]$ (Found: C, 34.20; H, 6.45; N, 11.95; S, 17.70; Tc, 26.80. $C_{10}H_{22}N_3S_2Tc$ requires C, 34.55; H, 6.40; N, 12.10; S, 18.40; Tc, 28.50%); ν(Tc≡N) 1065 and ν(NH) 3000–3150 cm^{-1} (KBr).

Synthesis of Oxotechnetium(v) *Complexes* $[TcO(L^n)]^+$ (n = 1 **1a** *or* 2 **1b**), $[TcO(H_2L^n)]^+$ (n = 3 **1c** *or* 4 **1d**) *and* $[TcO(HL^n)]$ (n = 3 **1e** *or* 4 **1f**).—To a methanolic solution of $[AsPh_4][TcOCl_4]$ (0.24 mmol in 5 cm^3) was added a solution of the hydrochloride salt of the ligand (0.30 mmol) and the pH was adjusted to 9 with 1 mol dm^{-3} aqueous NaOH. The solution rapidly became orange-red and was stirred at room temperature for a few minutes. Orange crystals were obtained by slow evaporation in air. Suitable crystals of **1a** for X-ray diffraction were obtained by addition of $NaBPh_4$ to a solution of the chloride salt of the complex in CH_2Cl_2–EtOH. Diffraction-quality crystals were also obtained for complex **1b** without adding $NaBPh_4$. To an orange solution of complex **1c** or **1d** in CH_2Cl_2–EtOH (0.23 mmol) was added 1 mol dm^{-3} aqueous NaOH until pH 12.5. By slow evaporation in air of the organic solvent orange plates of the neutral complexes **1d** and **1e** were formed. All the complexes were washed with ethanol and diethyl ether (yield 90%).

The same complexes were also obtained by starting with a solution of the complex $[TcCl_4(PPh_3)_2]$ (0.3 mmol) in CH_2Cl_2

(40 cm^3). An aqueous alkaline solution (pH 9.5) of the ligand (0.38 mmol) was added and vigorously stirred at room temperature until the colour turned from green to orange. The mixture was allowed to stand for a few minutes, the organic phase extracted, EtOH (5 cm^3) added, whereupon yellow orange needles of the complexes formed upon slow evaporation in air. The yield (40%) was however lower than that obtained with the previously described procedure. Conductivity measurements were performed in $MeNO_2$ and MeCN solution at 20 °C.

$[TcO(L^1)][BPh_4]$ (Found: C, 62.60; H, 6.80; N, 3.70; S, 8.20; Tc, 12.90. $C_{38}H_{50}BN_2OS_2Tc$ requires C, 62.95; H, 6.95; N, 3.85; S, 8.85; Tc, 13.70%); ν(Tc=O) 960 cm^{-1} (KBr); Λ 75 S cm^2 mol^{-1} ($MeNO_2$, 5 × 10^{-4} mol dm^{-3}). $\delta_H(CD_3NO_2)$ 4.2–4.5 (4 H, m, CH_2CH_3), 1.5 (6 H, t, CH_2CH_3), 1.7–1.9 (12 H, s, CMe_2) and 2.55–3.90 (8 H, d, CH_2NCH_2).

$[TcO(L^2)][BPh_4]$ (Found: C, 62.20; H, 6.55; N, 3.85; S, 8.90; Tc, 13.70. $C_{36}H_{46}BN_2OS_2Tc$ requires C, 62.05; H, 6.55; N, 4.00; S, 9.20; Tc, 14.20%); ν(Tc=O) 960 cm^{-1} (KBr); Λ 82 S cm^2 mol^{-1} ($MeNO_2$, 4.5 × 10^{-4} mol dm^{-3}). $\delta_H(CD_3NO_2)$ 1.65, 1.75, 1.90 and 2.05 (12 H, s, CMe_2) and 2.46–3.70 (6 H, s, NMe).

$[TcO(H_2L^3)]Cl$ (Found: C, 38.20; H, 6.70; N, 6.15; S, 13.95; Tc, 21.30. $C_{14}H_{30}ClN_2OS_2Tc$ requires C, 38.10; H, 6.90; N, 6.35; S, 14.50; Tc, 22.50%); ν(Tc=O) 955 and ν(NH) 2500–2700 cm^{-1} (KBr); Λ 110 S cm^2 mol^{-1} ($MeNO_2$ 1 × 10^{-4} mol dm^{-3}).

$[TcO(H_2L^4)]Cl$ (Found: C, 31.30; H, 5.65; N, 7.15; S, 15.90; Tc, 24.85. $C_{10}H_{22}ClN_2OS_2Tc$ requires C, 31.20; H, 5.75; N, 7.30; S, 16.60; Tc, 25.70%); ν(Tc=O) 955 and ν(NH) 2500–2700 cm^{-1} (KBr); Λ 115 S cm^2 mol^{-1} ($MeNO_2$ 5 × 10^{-5} mol dm^{-3}).

$[TcO(HL^3)]$ (Found: C, 41.30; H, 7.35; N, 6.70; S, 14.50; Tc, 23.20. $C_{14}H_{29}N_2OS_2Tc$ requires C, 41.55; H, 7.20; N, 6.90; S, 15.80; Tc, 24.50%); ν(Tc=O) 890 and ν(NH) 3150 cm^{-1} (KBr); Λ 7 × 10^{-4} S cm^2 mol^{-1} (MeCN 1 × 10^{-3} mol dm^{-3}).

$[TcO(HL^4)]$ (Found: C, 34.60; H, 6.00; N, 7.55; S, 16.95; Tc, 27.10. $C_{10}H_{21}N_2OS_2Tc$ requires C, 34.50; H, 6.10; N, 8.00; S, 18.40; Tc, 28.40%); ν(Tc=O) 890 and ν(NH)3160 cm^{-1} (KBr); Λ 9 × 10^{-4} S cm^2 mol^{-1} (MeCN 5 × 10^{-4} mol dm^{-3}).

Crystallography.—Crystal data. $C_{38}H_{50}BN_2OS_2Tc$, **1a** M = 724.20, orthorhombic, space group $P2_12_12_1$, a = 14.293(2), b = 14.936(6), c = 17.202(4) Å, U = 3672(2) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), Z = 4, D_c = 1.31 g cm^{-3}, μ = 5.9 cm^{-1}, $F(000)$ = 1520, crystal dimensions 0.17 × 0.19 × 0.26 mm.

$C_{14}H_{30}ClN_2OS_2Tc$ **1c**, M = 440.70, monoclinic, space group $P2_1/c$, a = 12.153(1), b = 12.917(3), c = 12.410(2) Å, β = 94.76(1)°, U = 1941.4(6) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), Z = 4, D_c = 1.51 g cm^{-3}, μ = 5.9 cm^{-1}, $F(000)$ = 912, crystal dimensions 0.31 × 0.42 × 0.52 mm.

Data collection and processing. CAD4 diffractometer, ω–2θ mode, graphite-monochromated Mo-Kα radiation: complex **1a**, 4421 unique reflections measured ($2 \leqslant \theta \leqslant 27°$), giving 2133 with $I \geqslant 3\sigma(I)$, corrected for absorption (minimum transmission factor: 0.98); **1c**, 4224 unique reflections measured ($2 \leqslant \theta \leqslant 27°$), giving 3673 with $I \geqslant 3\sigma(I)$, corrected for absorption (minimum transmission factor: 0.92).

Structure analysis and refinement. Solution by Patterson and Fourier methods. For complex **1a**, full-matrix least-squares refinement (in two blocks for final anisotropic cycles) with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. Atoms C(3) and C(4) were found to be disordered and refined in two positions. The weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + (0.05F_o^2)^2]$ gave satisfactory agreement analyses. Final R = 0.043 and R' = 0.048. Goodness of fit = 1.14. Final difference map peaks in the range ±0.3 e Å^{-3}. Final atomic coordinates are given in Table 1. For complex **1c**, hydrogen atoms found in F syntheses. Full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogens isotropic. The weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$ gave satisfactory agreement analyses. Final R = 0.021 and R' = 0.034. Goodness of fit = 1.35. Final atomic coordinates are given in Table 2 and selected bond distances and angles for both compounds in Table 3. Programs used and sources of scattering factor data are given in ref. 29.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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