Technetium(V) Nitrido Complexes with Tetra-azamacrocycles: Monocationic and Neutral Octahedral Complexes containing the $[Tc\equiv N]^{2+}$ Core. Crystal Structure of $[TcN(L^1)(H_2O)]\cdot 2H_2O$ (H_2L^1 = 1,4,8,11-tetra-azacyclotetradecane-5,7-dione)†

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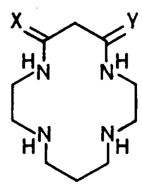
Neutral and monocationic complexes of technetium(V) containing the $[Tc\equiv N]^{2+}$ core have been synthesized by substitution reactions of $[TcNCl_2(PPh_3)_2]$ with tetra-azamacrocycles. The ligand 1,4,8,11-tetra-azacyclotetradecane-5-one has also been prepared. The complexes have been characterized by elemental analysis, i.r. and ^1H n.m.r. spectra, conductivity, and magnetic susceptibility measurements. The complex $[TcN(L^1)(H_2O)]\cdot 2H_2O$ (H_2L^1 = 1,4,8,11-tetra-azacyclotetradecane-5,7-dione) has a distorted octahedral structure with a H_2O molecule in *trans* position to the Tc≡N group. The quadridentate dianionic ligand forms with the Tc atom two *trans* five-membered and two *trans* six-membered metallacycles in which the Tc–N (sp^2) bond distances are significantly shorter than the corresponding Tc–N (sp^3) distances (2.051 *vs.* 2.127 Å).

In recent years the chemistry of metal complexes with macrocyclic ligands has been well documented, particularly from thermodynamic[1] and kinetic[2,3] points of view, but little work on technetium and rhenium complexes with this kind of ligand has been reported.

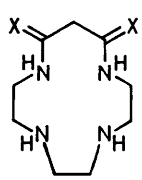
The chemistry of technetium complexes with open-chain and macrocyclic ligands has received more attention than that of rhenium because of the usage of complexes of ^{99m}Tc in diagnostic nuclear medicine. Recently, rhenium(V) dioxo complexes with acyclic tetramine ligands[4] and tetra-azamacrocycles[5] have been reported, but only the complex $[ReO_2(cyclam)]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) has been structurally characterized.[5] The chemistry of technetium(V) is dominated by $[Tc{=}O]^{3+}$ and *trans*-dioxo $[O{=}Tc{=}O]^+$ cores, the nature of the ligands determining the type of core. It was suggested[6,7] that Tc^V tends to form dioxo-octahedral complexes with nitrogen-donor ligands, *e.g.* as in $[TcO_2(cyclam)]^+$, $[TcO_2(en)_2]^+$, and $[TcO_2L]^+$ (en = ethylenediamine; L = 1,4-dithia-8,11-diazacyclotetradecane).[8–10]

With a series of amine–oxime ligands (L) both five-co-ordinate monoxo- and six-co-ordinate *trans*-dioxo-technetium(V) neutral species[11] [TcOL] and $[TcO_2L]$ were characterized for a better understanding of their chemistry as potential brain agents. Moreover, a number of monocationic complexes of technetium in low oxidation states such as $[Tc(P\text{–}P)_2Cl_2]^+$, $[Tc(P\text{–}P)_3]^+$ (P–P = bidentate diphosphine)[12] and $[Tc(RCN)_6]^+$ (R = alkyl or RCN = alkyl isocyanide)[13] were synthesized in order to obtain ^{99m}Tc myocardial agents,[14] but only the isocyanide complexes showed myocardial uptake in humans.[15]

In an alternative to the $[TcO]^{2+}$ and $[TcO_2]^+$ groups, Baldas and coworkers proposed the $[Tc\equiv N]^{2+}$ core[16] isoelectronic with $[Tc\equiv O]^{3+}$,[16a,b,17] in which the nitrido-ligand



H_2L^1 X = Y = O
HL^2 X = 2H, Y = O
L^4 X = Y = 2H (cyclam)



H_2L^3 X = O

(N^{3-}), a powerful π-electron donor, shows a high capacity to stabilize the metal in high oxidation state.[18] New technetium nitrido complexes as potential radiopharmaceutical agents[16a,c,17,19] containing the $[TcN]^{2+}$ functional moiety have been characterized and investigated. Recently, we reported a class of neutral nitrido complexes with bi- and tri-dentate Schiff bases derived from *S*-methyl dithiocarbazate[20] and new monocationic octahedral complexes with chelating amines.[21]

In this paper we report the synthesis and characterization of neutral and cationic technetium(V) nitrido complexes with cyclam and its derivatives, obtained by substitution reactions of $[TcNCl_2(PPh_3)_2]$ or by reduction of $[TcNX_4]^-$ (X = Cl or Br). We discuss the crystal structure of the complex $[TcN(L^1)$-

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Comparison of relevant distances (Å) (average) of some complexes of Tc and Re[a] with nitrogen-donor ligands

Complex	Ref.	Tc–N(amine)	Tc–N(amide)
$[TcO_2(en)_2]^+$	9	2.143—2.173	
$[TcO_2(cyclam]^+$	8	2.125	
$[ReO_2(cyclam)]^+$	5		
$[TcO(L)]^b$	11	2.088	1.913
$[TcO_2(L)]^b$	11	2.22	1.89
$[TcN(en)_2]^+$	21	2.156	
$[TcN(L')]^{+c}$	21	2.157	
$[TcN(L^1)]$	This work	2.127	2.051

[a] For $[ReO_2(cyclam)]^+$, av. Re–N(amine) 2.128—2.135 Å. [b] L = Amine–oxime ligand. [c] L′ = 4,7-diazadecane-1,10-diamine.

$(H_2O)]\cdot 2H_2O$ (H_2L^1 = 1,4,8,11-tetra-azacyclotetradecane-5,7-dione) in which the two deprotonated amide groups are *cis* to each other.

Results and Discussion

The square-pyramidal complex $[TcNCl_2(PPh_3)_2]$ reacts very easily with neutral or anionic tetra-azamacrocycles by simple substitution reactions in CH_2Cl_2–EtOH solution. The reaction is formally stoicheiometric and neutral or charged six-co-ordinated complexes are isolated. When the starting technetium compound is $[TcNCl_4]^-$, the addition of PPh_3 to the reaction mixture as reductant is required. If no counter ion is added the corresponding chloride salts [TcN(cyclam)Cl]Cl and $[TcN(L^2)(H_2O)]Cl$ are obtained. The characterization of the complexes is supported by elemental analyses, i.r. and ^1H n.m.r. spectra, conductivity, and magnetic susceptibility measurements (see Experimental section).

Conductivity data show that $[TcN(cyclam)Cl][BPh_4]$ and $[TcN(L^2)(H_2O)]Cl$ complexes carry a positive charge,[22] while magnetic susceptibility data reveal that all the complexes are diamagnetic, supporting a d^2 closed-shell configuration characteristic of the $[Tc{\equiv}N]^{2+}$ core.[23] I.r. spectra are very similar to those reported in our previous paper;[21] the N–H stretching bond falls in the range of 3 100—3 300 cm^{-1}; ν(Tc≡N) for all complexes is found in the range 1 070—1 090 cm^{-1} and is comparable with those recently reported for other technetium nitrido complexes.[20] The i.r. spectra of mono-oxo- and dioxo-tetra-azamacrocycle complexes show a band at 1 550—1 675 cm^{-1} consistent with the presence of a C=O group in the ligands. No Tc–Cl stretching was observed for the $[TcN(cyclam)Cl]^+$ complex, indicating a very long Tc–Cl bond distance. Proton n.m.r. spectra of the complexes are difficult to interpret due to the presence of poorly resolved multiplets.

It is well known that the $[Tc{\equiv}N]^{3+}$ core is stabilized by charged ligands like halogen anions,[16b] while $[Tc{\equiv}N]^{2+}$ prefers bases like phosphine, arsine,[24] Schiff bases,[20] dithiocarbamates,[17a,25] and polyacyclic amines.[21] The chemistry of the Tc≡N bond is mainly characterized by the formation of square-pyramidal complexes,[16b,17a,20,24,25] while the first octahedral nitrido complex to be structurally characterized was $[TcN(NCS)_2(MeCN)(PPh_3)_2]$;[17b] more recently, octahedral complexes $[TcN(bipy)_2Br]^+$ [26] (bipy = 2,2′-bipyridyl) and $[TcN(amine)Cl]^+$ [21] have been studied. The last complexes have negatively charged ligands Cl^- or Br^- in *trans* position to the Tc≡N moiety.

In this paper we report another class of pseudo-octahedral technetium(V) nitrido complexes with tetra-azamacrocycles. With the neutral cyclam the strong demand to decrease the excess of positive charge on the $[Tc{\equiv}N]^{2+}$ core makes the Cl^- reside in *trans* position to the Tc≡N multiple bond, giving the cationic $[TcN(cyclam)Cl]^+$ complex where the four nitrogen atoms of cyclam are co-ordinated in the equatorial plane. Also, ligand L^2 gives rise to the cationic compound $[TcN(L^2)(H_2O)]^+$ through the deprotonated amide group and with a H_2O molecule at an apical position *trans* to the nitrido group. The dioxotetra-azamacrocyclic ligands possessing two amidic groups form directly the neutral $[TcN(L^1)(H_2O)]$ and $[TcN(L^3)(H_2O)]$ complexes also containing a H_2O molecule. The Tc≡N bond distance of 1.615 Å for the $[TcN(L^1)(H_2O)]\cdot 2H_2O$ complex is consistent with the triple bond M≡N (M=Re or Tc) distances found in complexes structurally characterized[16,17,19–21,25,27] and the Tc atom is displaced from the basal plane defined by the four nitrogen atoms by 0.52 Å.

Tetra-azamacrocycles seem to be the most appropriate ligands for understanding natural products such as the metalloporphyrins, vitamin B_{12}, and chlorophyll because it is the size of the cavity in the centre of the macrocycles which plays an important role in many properties of the complexes.

Studies carried out on metal complexes of substituted 14-membered tetra-azamacrocycles show that to minimize ligand strain energy the M–N distances should be about 2.07 Å[28] because a constrictive effect may be responsible for their large ligand field strengths.[29] The first complex of a saturated *N*-donor macrocycle to be studied crystallographically was the high-spin $[Ni(cyclam)Cl_2]$ in which the Ni–N bond lengths are 2.058 Å.[30] In the analogous high-spin $[Ni(cyclam)(H_2O)_2]^{2+}$ and $[Ni(cyclam)(NO_3)_2]$ complexes the Ni–N bond distances are 2.10 and 2.055 Å (average) respectively, while in the nickel(III) complex $[NiL^5Cl_2]^+$ (L^5 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) the Ni–N distances are shorter (1.997 Å).[31] Recently, it was observed that in nickel(II) oxocyclam complexes[32] the bond distance Ni–N(amide) is shorter (1.905 Å) than those for other Ni–NH bonds (1.93 Å); the four nitrogen atoms are coplanar and the Ni^{II} is in this plane because the oxocyclam ring is rather elastic and can be stretched to accommodate the central metal. Dioxotetra-azamacrocyclic ligands possess a relatively rigid structure when the two amide groups are deprotonated and produce strong ligand fields. Modification of the donor groups by two carbonyl functions might serve to increase the cation selectivities of tetra-azamacrocycles, as found for macrocyclic hexaethers.[33]

So far, the only structurally characterized complexes of technetium and rhenium with tetra-azamacrocycles belong to the same class of $[MO_2]^+$ complexes as $[MO_2(cyclam)]^+$ (M = Tc or Re);[5,8] the longest M–N distance found for any cyclam complex was observed in $[ReO_2(cyclam)]^+$ (2.128—2.135 Å), while in the analogous dioxotechnetium complex the average distance is 2.125 Å. In Table 1 are summarized the Tc–N(amide) and Tc–N(amine) bond lengths of some complexes with *N*-donor ligands and of $[ReO_2(cyclam)]^+$. Usually, the Tc–N(amine) bond distances fall in the range 2.0—2.30 Å, while the Tc–N(amide) bond lengths are shorter indicating a double-bond character of the two deprotonated sp^2-nitrogen atoms.[8,9] So in oxo- and dioxo-technetium(V) complexes with quadridentate amine–oxime ligands containing two deprotonated nitrogen atoms the Tc–N(amide) bond distances are shorter (1.90 Å) than those observed for the two Tc–NH bonds (2.088—2.259 Å),[11] and also for the complex reported here the Tc–N(amide) bond lengths are 2.051 as compared to 2.127 Å for Tc–NH. In dioxo- and nitrido-complexes with *N*-donor open-chain neutral ligands[4,9,21] the Tc–NH distances are longer than those in analogous macrocyclic complexes (see Table 1), and this can be explained by taking into account the so-called macrocyclic effect.[33]

In summary, it appears that when the ligands are neutral, poor π donors, like amines or cyclam, octahedral dioxo complexes of Tc^V and Re^V are formed, while with good π

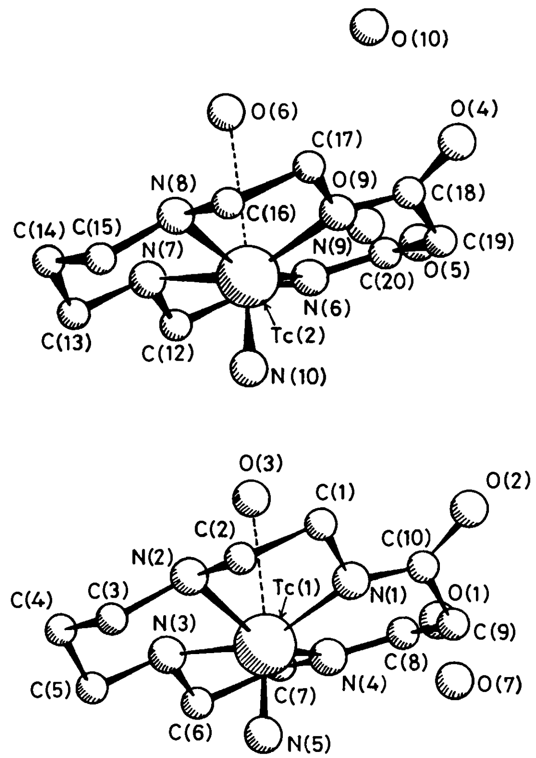


Figure 1. A perspective view of the asymmetric unit

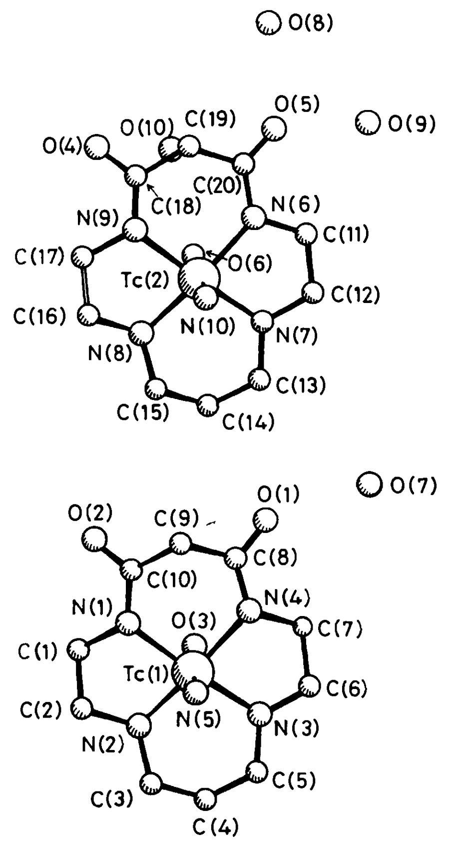


Figure 2. Another view of the asymmetric unit

donors, negatively charged ligands, five-co-ordination is preferred; in technetium(V) nitrido complexes the same trend is observed.

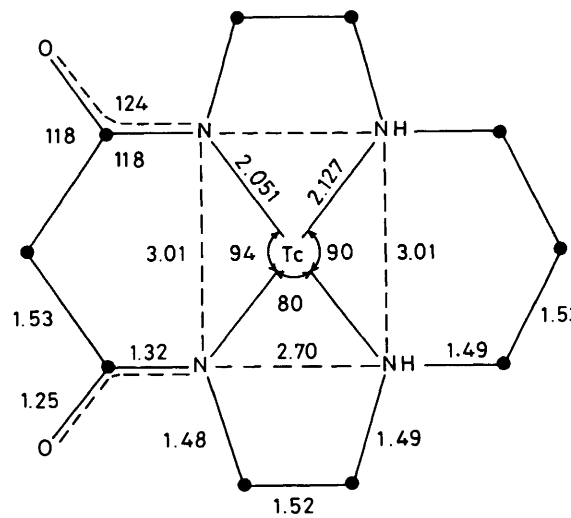


Figure 3. Structural details (distances in Å, angles in°) of the crown moiety. Mean values are reported

Description of the Structure of [TcN(L[1])(H_2O)]·$2H_2O$.—As shown in Figures 1 and 2 the two independent molecules of the compound are chemically and structurally equivalent. The Tc atom is six-co-ordinated in a rather distorted octahedral geometry, being directly bound to four N atoms from the macrocyclic ligand in the equatorial plane and to one nitrido N atom and to one water molecule in axial positions. While the equatorial N atoms are approxomately coplanar (within 0.008 Å) the metal atom is displaced by 0.52 Å from the basal plane towards the nitrido-nitrogen atom, probably because of repulsion effects of this strongly bound atom on the adjacent nitrogens of the ligands. Moreover, the N(nitrido)–Tc–O angle is only approximately linear (174°). Deviations from idealized octahedral geometry arise due to the fact that the Tc atom is involved in the formation of two *trans* five-membered and two *trans* six-membered metallacycles, which has influence both on the N • • • N bites as well as on the N–Tc–N angles (see Figure 3). It should be noted that all structural details in the two molecules are fully comparable, with negligible differences. Bond lengths clearly indicate a strong double-bond character for the contiguous CO and CN groups, with delocalization among these atoms of the π-electron density. Moreover, the Tc–N(sp^2) bond distances are significantly shorter than the corresponding Tc–N(sp^3) distances (2.051 *vs.* 2.127 Å); for comparison, a Tc–N(sp^3) bond distance of 2.125(11) Å (mean of four values) was found in the octahedral complex *trans*-[TcO_2(cyclam)]$^+$.[8] Some double-bond character cannot be excluded also for the Tc–N(sp^2) bonds, in which case the entire O⋯C⋯N⋯Tc sequences would be involved in the observed delocalization. In addition, the presence of the four sp^2-hybridized atoms results in the six-membered metallacycles being approximately planar, while the opposite six-membered cycles, where all C and N atoms are sp^3 hybridized, adopt the characteristic chair configuration.

Other C–N bonds are single, the mean 1.483 Å found for Tc–N distances involving four-co-ordinated nitrogen atoms being slightly longer than a mean of 1.475 Å for three-co-ordinated nitrogen atoms. This seems surprising if one takes into account the corresponding values of 1.479(5) and 1.472(5) Å reported by Sutton for these bonds.[34] As far as the nitrido Tc≡N bond is concerned, the observed mean value of 1.615 Å indicates the presence of considerable triple-bond character[35] and can be compared with the corresponding metal–nitrido distances found in complexes of Re^V[36] and Tc^V[16,17a,19–21,25,27] (the atomic radius of Re and Tc is the same[37]): 1.660(8) Å in

Table 2. Atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for compound (**1a**)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Tc(1)	0.103 42(3)	0.053 42(3)	0.155 55(1)	N(7)	0.408 7(3)	0.850 4(4)	0.598 4(1)
N(1)	0.256 0(3)	0.160 6(3)	0.184 1(1)	N(8)	0.479 7(3)	0.972 4(3)	0.690 3(1)
N(2)	−0.004 4(3)	0.174 1(3)	0.199 3(1)	N(9)	0.735 8(3)	0.968 4(3)	0.670 2(1)
N(3)	−0.066 6(3)	0.030 6(4)	0.110 8(1)	N(10)	0.587 3(4)	0.723 1(4)	0.667 0(1)
N(4)	0.194 0(3)	0.018 9(3)	0.094 8(1)	O(4)	0.930 2(3)	1.073 6(3)	0.663 8(1)
N(5)	0.103 9(4)	−0.080 1(4)	0.183 4(1)	O(5)	0.829 2(3)	0.883 5(4)	0.530 1(1)
O(1)	0.363 4(3)	0.062 4(3)	0.048 0(1)	O(6)	0.543 1(4)	1.113 1(4)	0.597 4(1)
O(2)	0.448 7(3)	0.265 8(3)	0.173 4(1)	C(11)	0.572 5(5)	0.817 8(6)	0.539 9(2)
O(3)	0.073 4(3)	0.273 6(3)	0.108 2(1)	C(12)	0.444 7(5)	0.768 3(6)	0.558 8(2)
C(1)	0.215 3(4)	0.257 3(4)	0.217 9(2)	C(13)	0.291 8(5)	0.806 3(6)	0.622 8(2)
C(2)	0.087 8(4)	0.211 9(4)	0.238 2(1)	C(14)	0.258 3(5)	0.898 3(6)	0.661 3(2)
C(3)	−0.128 9(4)	0.113 1(5)	0.213 0(2)	C(15)	0.356 1(5)	0.909 5(5)	0.703 2(2)
C(4)	−0.222 3(4)	0.087 1(5)	0.170 9(2)	C(16)	0.576 2(5)	1.000 7(5)	0.729 1(2)
C(5)	−0.182 6(4)	−0.013 1(5)	0.135 9(2)	C(17)	0.701 2(5)	1.050 7(5)	0.709 2(2)
C(6)	−0.027 3(5)	−0.056 3(5)	0.072 8(1)	C(18)	0.848 0(4)	0.991 5(4)	0.650 4(2)
C(7)	0.102 2(4)	−0.005 4(5)	0.055 2(1)	C(19)	0.885 2(5)	0.904 1(5)	0.610 6(2)
C(8)	0.316 3(4)	0.052 4(4)	0.087 5(1)	C(20)	0.787 6(5)	0.877 6(4)	0.569 9(2)
C(9)	0.407 9(4)	0.075 6(4)	0.129 9(2)	O(7)	0.366 4(4)	−0.052 1(5)	0.962 9(1)
C(10)	0.369 0(4)	0.176 3(4)	0.164 3(1)	O(8)	−0.098 4(5)	0.356 5(5)	0.989 5(2)
Tc(2)	0.583 14(4)	0.861 90(4)	0.642 08(1)	O(9)	0.275 8(4)	0.109 3(5)	0.560 3(1)
N(6)	0.666 0(3)	0.844 4(4)	0.579 2(1)	O(10)	0.231 8(5)	0.761 6(5)	0.434 3(2)

Table 3. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for compound (**1a**)

Tc(1)–N(1)	2.054(4)	Tc(2)–N(6)	2.048(4)	N(1)–Tc(1)–N(2)	80.6(2)	N(6)–Tc(2)–N(7)	80.4(2)
Tc(1)–N(2)	2.128(4)	Tc(2)–N(7)	2.130(4)	N(2)–Tc(1)–N(3)	90.2(2)	N(6)–Tc(2)–N(9)	93.8(2)
Tc(1)–N(3)	2.121(3)	Tc(2)–N(8)	2.126(4)	N(1)–Tc(1)–N(4)	94.6(2)	N(7)–Tc(2)–N(8)	89.8(2)
Tc(1)–N(4)	2.054(3)	Tc(2)–N(9)	2.046(4)	N(3)–Tc(1)–N(4)	80.9(2)	N(8)–Tc(2)–N(9)	80.3(2)
Tc(1)–N(5)	1.612(4)	Tc(2)–N(10)	1.621(4)	N(5)–Tc(1)–N(1)	106.6(2)	N(10)–Tc(2)–N(6)	108.2(2)
Tc(1)–O(3)	2.688(4)	Tc(2)–O(6)	2.947(4)	N(5)–Tc(1)–N(2)	101.8(2)	N(10)–Tc(2)–N(7)	102.6(2)
N(1)–C(1)	1.479(6)	N(6)–C(11)	1.473(6)	N(5)–Tc(1)–N(3)	101.0(2)	N(10)–Tc(2)–N(8)	101.4(2)
C(1)–C(2)	1.521(6)	C(11)–C(12)	1.522(7)	N(5)–Tc(1)–N(4)	106.6(2)	N(10)–Tc(2)–N(9)	107.8(2)
C(2)–N(2)	1.482(6)	C(12)–N(7)	1.492(7)	O(3)–Tc(1)–N(1)	78.7(1)	O(6)–Tc(2)–N(6)	75.1(1)
N(2)–C(3)	1.486(6)	N(7)–C(13)	1.483(7)	O(3)–Tc(1)–N(2)	75.3(1)	O(6)–Tc(2)–N(7)	72.3(1)
				O(3)–Tc(1)–N(3)	73.5(1)	O(6)–Tc(2)–N(8)	75.1(2)
C(3)–C(4)	1.532(7)	C(13)–C(14)	1.523(8)	O(3)–Tc(1)–N(4)	76.1(1)	O(6)–Tc(2)–N(9)	77.1(2)
C(4)–C(5)	1.526(7)	C(14)–C(15)	1.535(7)	O(3)–Tc(1)–N(5)	173.7(2)	O(6)–Tc(2)–N(10)	173.6(2)
C(5)–N(3)	1.484(6)	C(15)–N(8)	1.480(6)	Tc(1)–N(1)–C(1)	114.2(4)	Tc(2)–N(6)–C(11)	115.2(4)
N(3)–C(6)	1.496(6)	N(8)–C(16)	1.486(6)	Tc(1)–N(1)–C(10)	123.3(3)	Tc(2)–N(6)–C(20)	125.7(4)
C(6)–C(7)	1.526(7)	C(16)–C(17)	1.512(7)	Tc(1)–N(2)–C(2)	106.6(3)	Tc(2)–N(7)–C(12)	105.2(4)
C(7)–N(4)	1.464(5)	C(17)–N(9)	1.474(6)	Tc(1)–N(2)–C(3)	111.8(3)	Tc(2)–N(7)–C(13)	113.5(4)
N(4)–C(8)	1.317(5)	N(9)–C(18)	1.321(6)	Tc(1)–N(3)–C(5)	112.3(3)	Tc(2)–N(8)–C(15)	112.0(3)
C(8)–C(9)	1.523(6)	C(18)–C(19)	1.531(7)	Tc(1)–N(3)–C(6)	106.2(3)	Tc(2)–N(8)–C(16)	115.7(4)
C(9)–C(10)	1.515(6)	C(19)–C(20)	1.527(7)	Tc(1)–N(4)–C(7)	114.1(3)	Tc(2)–N(9)–C(17)	114.7(4)
C(10)–N(1)	1.317(5)	C(20)–N(6)	1.321(6)	Tc(1)–N(4)–C(8)	123.6(4)	Tc(2)–(N(9)–C(18)	125.5(4)
C(8)–O(1)	1.263(5)	C(18)–O(4)	1.246(6)				
C(10)–O(2)	1.257(5)	C(20)–O(5)	1.249(6)				

Table 4. Possible hydrogen bond distances (Å)

O(10) ··· O(7^{I})	2.69	O(9) ··· O(3^{VII})	2.81
O(7) ··· O(1^{II})	2.74	O(10) ··· O(8^{VIII})	2.82
O(4) ··· O(3^{III})	2.74	O(10) ··· O(6^{IX})	2.83
O(6) ··· O(2^{IV})	2.76	O(8) ··· O(5^{X})	2.86
O(7) ··· O(1^{V})	2.78	O(9) ··· O(6^{XI})	2.87
O(9) ··· O(5^{VI})	2.78		

Symmetry codes: I $x, \frac{1}{2} - y, -\frac{1}{2} + z$; II $x, y, 1 + z$; III $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$; IV $x, \frac{3}{2} - y, \frac{1}{2} + z$; V $1 - x, \bar{y}, 1 - z$; VI $1 - x, 1 - y, 1 - z$; VII $x, \frac{1}{2} + y, \frac{1}{2} + z$; VIII $x, \frac{1}{2} + y, \frac{3}{2} - z$; IX $1 - x, 2 - y, 1 - z$; X $1 - x, -\frac{1}{2} - y, \frac{3}{2} - z$; XI $x, -1 + y, z$.

[$ReNCl_2(PMe_2Ph)_3$] and 1.602(9) Å in [$ReNCl_2(PPh_3)_2$] (in the latter compound the Re atom is five-co-ordinated).

As shown in Table 4, where O ··· O contacts less than 3.0 Å are reported, a rather complicated network of hydrogen bonds supplies stability and compactness to the crystal packing. In general, each ketonic oxygen of the complex molecule forms at least one hydrogen bond with the clathrate solvent or with the co-ordinated water of another complex molecule, each co-ordinated water [O(3) and O(6)] being *trans* hydrogen bonded to one ketonic oxygen [O(4) and O(2) respectively] and to the bridging O(9) water molecule. Final atomic parameters are listed in Table 2 bond distances and angles in Table 3.

Experimental

Materials.—Technetium-99 is a weak β emitter (0.292 kEv, *ca.* 4.7 × 10^{-17} J; $t_{\frac{1}{2}}$ = 2.12 × 10^5 y) and all manipulations were carried out in a laboratory approved for low-level radioactivity. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. All common laboraotory chemicals were of reagent grade and were used without purification. Technetium, as aqueous

$NH_4[^{99}TcO_4]$, was purchased from the Radiochemical Centre, Amersham.

The $[AsPh_4]^+$ salt of the tetrachloronitridotechnetate(VI) anion $[TcNCl_4]^-$ and $[TcNCl_2(PPh_3)_2]$ were prepared as reported,[16a] 1,4,8,11-tetra-azacyclotetradecane (cyclam) was purchased from Aldrich Chemicals, 1,4,8,11-tetra-azacyclotetradecane-5,7-dione (HL_2^1) and 1,4,7,10-tetra-azacyclotridecane-11,13-dione(H_2L^3) were synthesized according to the literature procedures.[38]

I.r. spectra were recorded on a Perkin-Elmer 599 grating spectrometer using KBr pellets. Elemental analyses were performed on a Carlo Erba elemental analyzer model 1106, except for radioactive technetium which were carried out on a Packard liquid-scintillation instrument, model TRICARB 300C, with Imstagel as scintillator, after dissolution of the samples in hydrogen peroxide–nitric acid solutions. Proton n.m.r. spectra of MeCN and $CHCl_3$ solutions were collected on a Varian Gemini 300 spectrometer with $SiMe_4$ as internal standard. Magnetic susceptibility measurements were made by the Evans method.[39] Conductivity measurements were performed in $MeNO_2$ and MeCN solutions with use of an Amel model 134 conductivity meter at 20 °C.

Synthesis of 1,4,8,11-*tetra-azacyclotetradecane*-5-*one*-(HL^2).—This ligand was prepared by condensation of ethyl 3-bromopropionate (5 g, 3.125 mmol) and 1,4,8,11-tetra-aza-undecane (5.65 g, 3.125 mmol) in ethanol (500 cm³) and refluxed from 3 to 5 d. The solution was concentrated to small volume, and the product isolated by column chromatography using silica gel [eluant: chloroform–methanol–30% (ammonia–water) (6:4:1) $R_f = 0.5$]. The dihydrobromide salt of the ligand was recrystallized from 25% ethanol–water (Found: C, 32.20; H, 6.50; Br, 42.55; N, 15.10; O, 4.55. Calc. for $C_{10}H_{24}Br_2N_4$: C, 31.95; H, 6.45; Br, 42.50; N, 14.90; O, 4.25%); ν(CO) 1 660 and ν(NH) 3 200 cm^{-1} (Nujol).

Synthesis of the Complexes $[TcN(L^1)(H_2O)]\cdot 2H_2O$ (**1a**), $[TcN(L^2)(H_2O)]Cl\cdot 2H_2O$ (**1b**), *and* $[TcN(L^3)(H_2O)]\cdot H_2O$ (**1c**).—To a pink solution of $[TcNCl_2(PPh_3)_2]$ (0.28 mmol) in CH_2Cl_2–EtOH (3:1) heated at 40 °C was added dropwise a solution of the appropriate ligand in EtOH in the stoicheiometric ratio (1:1). After a few minutes the colour became light yellow. Heating was removed after 15 min and yellow crystals of the final products were recovered by slow evaporation of the solvent in air; they were washed with ethanol and dried with diethyl ether. Recrystallization was from CH_2Cl_2–EtOH.

$TcN(L^1)(H_2O)]\cdot 2H_2O$ (90%) (Found: C, 30.25; H, 6.20; N, 17.40; Tc, 24.35. $C_{10}H_{24}N_5O_5Tc$ requires C, 30.50; H, 6.15; N, 17.80; Tc, 25.20%; *M* 393.19); ν(CO) 1 660, 1 565; ν(NH) 3 380; ν(Tc≡N) 1 080; ν(CN) 1 050 cm^{-1} (KBr).

$TcN(L^2)(H_2O)]Cl\cdot 2H_2O$ (85%) (Found: C, 29.10; H, 6.40; N, 16.26; Tc, 23.10. $C_{10}H_{27}ClN_5O_4Tc$ requires C, 28.90; H, 6.55; N, 16.85; Tc, 23.80%; *M* 415.67); ν(CO) 1 650, 1 560; ν(NH) 3 140, 3 390; ν(Tc≡N) 1 090; ν(CN) 1 070 cm^{-1} (KBr); Λ 105 s cm² mol^{-1} (MeCN, 1.5 × 10^{-4} mol dm^{-3}, 20 °C).

$TcN(L^3)(H_2O)]\cdot H_2O$ (85%) (Found: C, 29.80; H, 5.45; N, 19.30; Tc, 26.55. $C_9H_{20}N_5O_2Tc$ requires C, 29.90; H, 5.60; N, 19.40; Tc, 27.40%; *M* 361.16); ν(CO) 1 640, 1 675; ν(NH) 3 380; ν(Tc≡N) 1 075; ν(CN) 1 060 cm^{-1} (KBr).

Synthesis of the complex $[TcN(L^4)(Cl)][BPh_4]\cdot H_2O$ (**1d**).—Complex (**1d**) was obtained following the same procedure as above, but at the end of the heating an ethanolic solution of $NaBPh_4$ (0.1g, 5 cm³) was added. If the reaction solution was left to evaporate in air without adding $NaBPh_4$ the corresponding salt [TcN(cyclam)Cl]Cl was isolated as a yellow powder.

$[TcN(L^4)Cl][BPh_4]\cdot H_2O$ (90%) (Found: C, 59.30; H, 6.60; N, 9.90; Tc, 13.80. $C_{34}H_{46}BClN_5OTc$ requires C, 59.50; H, 6.75; N, 10.20; Tc, 14.45%; *M* 685.63); ν(NH) 3 220, 3 060; ν(Tc≡N) 1 090; ν(CN) 1 070 cm^{-1} (KBr); Λ 122 s cm² mol^{-1} (CH_3NO_2, 6 × 10^{-5} mol dm^{-3} 20 °C).

The same compounds can also be prepared using the $[AsPh_4]^+$ salt of $[TcNX_4]^-$ (X = Cl or Br), but adding a three-fold molar excess of triphenylphosphine in ethanol–methylene chloride solution (1:3, 20 cm³). All the complexes are stable in the solid state.

Crystal Structure Determination for $[TcN(L^1)(H_2O)]\cdot 2H_2O$ (**1a**).—Crystals were obtained as described in the corresponding synthesis.

Crystal data. $C_{10}H_{24}N_5O_5Tc$, $M = 393$, monoclinic, $a = 10.154(5)$, $b = 10.453(5)$, $c = 28.937(4)$ Å, $\beta = 92.69(3)°$, $U = 3\,068$ Å³ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/c$ (alternative $P2_1/c$, no. 14), $Z^* = 8$, $D_c = 1.48$ g cm^{-3}, crystal dimensions, a fragment of maximum dimension 0.2 mm was selected, μ (Mo-K_α) = 9.3 cm^{-1}, $F(000) = 1\,616$.

Data collection and processing. Philips diffractometer with graphite-monocromated Mo-K_α radiation; intensities were measured using the θ—2θ scan method with a scan speed 2° min^{-1}, between 2 and 25°, yielding 5 853 independent reflections, 4 083 with $I \geqslant 3\sigma(I)$; data corrected for Lorentz and polarization absorption.

Structure analysis and refinement. Solution by Patterson and Fourier methods. Refinement of scale-factor, positional, and thermal parameters converged to give the final conventional agreement index *R* 0.031. Maximum and minimum heights in a final Fourier difference map were 0.61 and −0.56 e Å⁻³. Full-matrix least-squares minimization of the function $\Sigma w(\Delta F)^2$ with $w = 1$. The asymmetric unit of the cell contains, in addition to the two independent molecules of the complex, also four molecules of H_2O present as a clathrate solvent. The positions of the H atoms were determined from electron-density maps and were refined with fixed isotropic thermal parameters ($U = 0.07$ Å²). Programs used and sources of scattering factor data are given in ref. 40.

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

* There are two independent molecules in the asymmetric unit, so that there are eight molecules in the elementary cell. Perhaps, taking in account that the position of the four clathrate water molecules in the asymmetric position of the cell is not the same with respect to the complex molecules, the compound could be more correctly formulated as $2[TcN(L^1)(H_2O)]\cdot 4H_2O$, and in this case there would be only four 'formula units' in the unit cell ($Z = 4$). However, because the molecules of the complex can be considered fully equivalent (see text) from chemical and structural points of view, and their structure not influenced by the clathrate solvent, even the simplified adopted formulation $[TcN(L^1)(H_2O)]\cdot 2H_2O$ seems acceptable.

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