Synthesis of Six-co-ordinate Technetium(V) Complexes with *N*-Phenylsalicylideneimine. *X*-Ray Crystal Structure of Chloro-oxobis(*N*-phenylsalicylideneiminato)technetium(V)*

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The complexes [TcOClL$^1_2$] (1) and [AsPh$_4$][TcOCl$_3$L^1] (2) (HL^1 = *N*-phenylsalicylideneimine) of the long-lived isotope technetium-99 were synthesized starting from [AsPh$_4$][TcOCl$_4$]. The characterization was performed by elemental analysis of technetium and chlorine and i.r. spectra. The crystal structure of (1) has been determined and refined from 1 259 diffractometer data (up to 2θ = 44°) to a final *R* of 0.057. Crystals are monoclinic, space group $P2_1/n$, with unit-cell dimensions *a* = 12.854(4), *b* = 15.840(7), *c* = 11.433(4) Å, β = 93.43(2)°, and *Z* = 4. The co-ordination around Tc is approximately octahedral with the two chelate ligands mutually orthogonal, one ligand bridging an equatorial and an apical position and the other two, equatorial ones. The equatorial plane is completed by the Cl atom and the other apical position is occupied by the O atom strongly bonded to Tc [Tc–O 1.67(1) Å]. The simple method of synthesis, the short reaction time, and the versatility of this type of Schiff base ligand is of importance in the design of technetium-99m labelled radiopharmaceuticals containing N and O co-ordinating centres.

Since Cotton *et al.*[1] determined unequivocally, by *X*-ray crystal analysis, the formulation of [TcOCl$_4$]$^-$, this compound has been established as a very good starting material in the synthesis of a large number of complexes with a variety of organic ligands.[2–4] However, the method of synthesis of [TcOCl$_4$]$^-$ was simplified by Davison *et al.*[3] with the aim of using this pre-reduced complex in the synthesis of Tc radiopharmaceuticals. This paper outlines a simpler method for the synthesis of [TcOCl$_4$]$^-$ and the synthesis and characterization of two six-co-ordinate Tc^V complexes, [TcOClL$^1_2$] (1) and [AsPh$_4$][TcOCl$_3$L^1] (2), with the *N*-phenylsalicylideneiminate ligand L^1, which can be the first of a series of complexes with Schiff base ligands very important in the preparation of new radiopharmaceuticals labelled with ^{99m}Tc. In addition, we report and discuss here the *X*-ray crystal structure of the neutral complex (1).

Experimental

Elemental Analyses.—Analysis for chlorine was performed by the method reported previously,[5] while technetium was determined by the liquid scintillation method.

Materials.—Technetium as [NH$_4$][^{99}TcO$_4$] in 0.1 mol dm^{-3} ammonia solution was purchased from Amersham (England). [AsPh$_4$][TcO$_4$] was obtained by precipitating pertechnetate with [AsPh$_4$]Cl. *N*-Phenylsalicylideneimine (HL^1) was prepared by adding a stoicheiometric amount of aniline to an ethanol solution of salicylaldehyde. The solid obtained was filtered off and washed with ethanol and diethyl ether. Other reactants were reagent grade chemicals.

Apparatus.—Infrared spectra of samples as Nujol mulls between CsI discs were recorded on a Perkin-Elmer 580B spectrophotometer in the range 4 000—200 cm^{-1}.

Syntheses.—[AsPh$_4$][TcOCl$_4$]. [AsPh$_4$][TcO$_4$] (0.5 g) was added to ethanol (30 cm^3) and gaseous hydrochloric acid was bubbled into the mixture. The white starting compound became greenish and after 20 min an olive-green powder was filtered off. The solid was washed with ethanol. Yield 97%, based on Tc. Bubbling of HCl gas for a longer time does not affect the reaction. Recrystallization from CH$_2$Cl$_2$–pentane produced dark green plates.

[TcOClL$^1_2$] (1). [AsPh$_4$][TcOCl$_4$] (0.1 g) was treated with an excess of *N*-phenylsalicylideneimine (0.09 g) in ethanol (30 cm^3) and boiled under reflux for 1 h. The solution became immediately orange and then darkened continuously to brown. On cooling, a violet-brown powder was produced. The solid was filtered off, washed with cold ethanol and diethyl ether, and dried. Recrystallization from CH$_2$Cl$_2$ gave dark violet prisms. Yield 95%, based on Tc. The compound is soluble in CH$_2$Cl$_2$, MeCN, and tetrahydrofuran, partially soluble in benzene and EtOH, and insoluble in diethyl ether and pentane (Found: Cl, 6.7; Tc, 18.45. Calc. for C$_{26}$H$_{20}$ClN$_2$O$_3$Tc: Cl, 6.55%; Tc. 18.2).

[AsPh$_4$][TcOCl$_3$L^1] (2). [AsPh$_4$][TcOCl$_4$] (0.1 g) was treated with an excess of *N*-phenylsalicylideneimine (0.06 g) in EtOH (20 cm^3) and stirred at room temperature for 4 h, or 10 min refluxing. After filtration of the solid residue (starting compound), the ethanol solution was treated with pentane and a dark orange powder was collected, washed with diethyl ether, and dried. Recrystallization from CH$_2$Cl$_2$–pentane gave a yellow-brown powder, yield 55%. The compound is soluble in EtOH, CH$_2$Cl$_2$, and MeCN, and insoluble in benzene, diethyl ether, and pentane (Found: Cl, 13.35; Tc, 12.25. Calc. for C$_{37}$H$_{30}$AsCl$_3$NTc: Cl, 13.3; Tc, 12.35%).

Crystal Data, Structure Determination, and Refinement of (1).—Details of crystal data, measurements of intensity, and processing are summarized in Table 1. Final atomic positional parameters are listed in Table 2. Calculated bond lengths and angles are in Table 3; some relevant least-squares planes and dihedral angles are reported in Table 4. If allowance is made for small differences between the two L^1 ligands, then only the phenyl C–C distances from C(23) to C(26) differ by more than one standard deviation, these being the atoms with the highest thermal motion, and this is not particularly significant. The atom numbering scheme is shown in the Figure.

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* *Supplementary data available* (No. SUP 23397, 15 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Crystallographic data, collection, and refinement for [$TcOClL^1_2$]

Molecular formula	$C_{26}H_{20}ClN_2O_3Tc$
Molecular weight	528.8
Crystal dimensions/mm	0.13 × 0.20 × 0.09
Crystal system	monoclinic
Space group	$P2_1/n$
Cell constants (at 25 °C) (Mo-K_α radiation λ = 0.7107 Å)	a = 12.854(4) Å b = 15.840(7) Å c = 11.433(4) Å β = 93.43(2)° U = 2 323.7 Å^3
Z	4
F(000)	1 096
μ/cm^{-1}	6.8
Automatic diffractometer	Philips PW1100
Scanning range for 2θ	3—44°
Scan width for each reflection	$\Delta 2\theta = 1.6 + 0.3\tan\theta$
Scan speed	0.04° s^{-1}
Background time	20 s
Maximum standard deviations	5%
Independent reflections	3 011
Reflections, $I > 3\sigma(I)$	1 259
Weighting scheme	$w = 1$
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Final $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.057
Peaks in the final ΔF	No greater than 0.6 e Å^{-3}
Neutral-atom scattering factors	*a*
Anomalous dispersion	*b*
Data reduction	*c*
Structure determination and refinement	*d*

[a] D. T. Cromer and J. R. Waber, *Acta Crystallogr.*, 1965, **18**, 104. [b] D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1891. [c] B. M. Gatehouse and B. K. Miskin, *Acta Crystallogr., Sect. B*, 1974, **30**, 1311, 2112. [d] J. M. Stewart, *X*-RAY System, Technical Report TR-192, Computer Science Centre, University of Maryland, 1972.

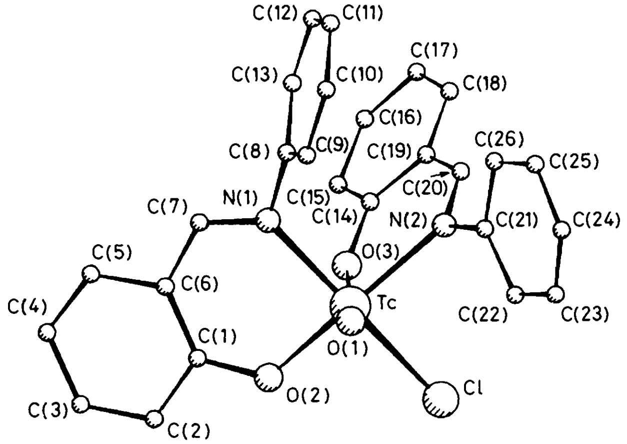

Figure. View of [$TcOClL^1_2$] showing the atom numbering system

Table 2. Fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Tc	2 017(1)	3 206(1)	1 830(1)
Cl	2 911(4)	3 677(3)	3 597(4)
O(1)	2 850(8)	3 497(7)	837(10)
O(2)	1 126(8)	4 231(7)	1 927(10)
O(3)	992(8)	2 651(7)	2 750(9)
N(1)	1 031(10)	2 736(9)	428(12)
N(2)	2 825(10)	1 992(8)	2 013(11)
C(1)	162(13)	4 321(11)	1 441(16)
C(2)	−336(12)	5 077(11)	1 775(14)
C(3)	−1 349(15)	5 217(12)	1 342(17)
C(4)	−1 888(15)	4 653(12)	594(17)
C(5)	−1 396(14)	3 910(11)	308(16)
C(6)	−374(14)	3 751(12)	719(16)
C(7)	95(13)	3 011(10)	187(14)
C(8)	1 337(13)	2 022(11)	−257(15)
C(9)	2 176(14)	2 087(11)	−939(16)
C(10)	2 460(16)	1 387(14)	−1 569(19)
C(11)	1 959(18)	627(14)	−1 465(20)
C(12)	1 125(18)	541(14)	−768(21)
C(13)	792(15)	1 233(13)	−90(18)
C(14)	729(12)	1 849(13)	2 991(13)
C(15)	−244(13)	1 705(14)	3 451(15)
C(16)	−502(15)	875(14)	3 720(18)
C(17)	165(16)	213(13)	3 509(18)
C(18)	1 144(14)	371(12)	3 103(15)
C(19)	1 428(13)	1 175(11)	2 823(15)
C(20)	2 432(14)	1 298(12)	2 385(16)
C(21)	3 860(13)	1 959(11)	1 551(15)
C(22)	4 613(16)	2 527(13)	1 885(18)
C(23)	5 609(19)	2 453(17)	1 415(22)
C(24)	5 774(16)	1 834(17)	650(19)
C(25)	5 080(19)	1 251(15)	327(20)
C(26)	4 059(16)	1 292(13)	803(18)

Results and Discussion

The preparation of [$TcOCl_4$]$^-$ using HCl gas is a very simple and clean method of synthesis. The reaction probably occurs in solution but, as both the starting compound and the product are almost insoluble, pertechnetate reacts and solubilizes continuously while the [$TcOCl_4$]$^-$ species precipitates immediately out of the solution. In such a way further reactions cannot occur (*e.g.* the production of [$TcCl_6$]$^{2-}$). Also, the reaction time is very short and this is very important when [$TcOCl_4$]$^-$ is used as a pre-reduced compound in the preparation of ^{99m}Tc radiopharmaceuticals. The characterization of [$AsPh_4$][$TcOCl_4$] confirms literature data available [*e.g.* ν(Tc=O) 1 020 cm^{-1}] and shows the purity of the compound.

The synthesis of the complex [$TcOClL^1_2$] is also very simple. The complex is air stable both in the solid and in solution. The characterization was performed by elemental analyses of Tc and Cl, by i.r. spectroscopy, and definitely confirmed by *X*-ray analysis. The i.r. spectrum of this compound was compared with that of the analogue, [$ReOClL^2_2$] (L^2 = *N*-methylsalicylideneiminate),[6] see Table 5. The fingerprinting of the spectrum of the technetium compound in the range 2 000—200 cm^{-1} is very similar to the rhenium analogue, in particular for [$TcOClL^1_2$] ν(C=N) are at 1 618 and 1 603 cm^{-1} and ν(C−O) at 1 310 and 1 285 cm^{-1}, suggesting the co-ordination both of aldimine nitrogen and phenolic oxygen. The ν(Tc=O) vibration (940 cm^{-1}) is at lower frequency than ν(Re=O) (959 cm^{-1}). The band at 320 cm^{-1} for (1) was attributed to ν(Tc−Cl).

The intermediate compound [$TcOCl_3L^1$]$^-$ was obtained using short times or milder conditions. From this compound it

Table 3. Bond distances (Å) and angles (°)

(*i*) Around technetium

Tc–O(1)	1.67(1)	Tc–O(3)	1.94(1)	N(1)–Tc–O(3)	81.7(5)	O(2)–Tc–N(2)	168.7(5)	N(1)–Tc–N(2)	91.3(5)
Tc–O(2)	1.99(1)	Tc–N(2)	2.19(1)	O(3)–Tc–Cl	89.5(3)	O(1)–Tc–N(2)	89.3(5)	Cl–Tc–O(2)	87.0(3)
Tc–N(1)	2.12(1)	Cl–Tc–O(1)	101.4(4)	O(1)–Tc–O(3)	167.1(5)	O(1)–Tc–O(2)	101.9(5)	Cl–Tc–N(2)	89.5(3)
Tc–Cl	2.38(1)	O(1)–Tc–N(1)	87.8(5)	N(1)–Tc–Cl	171.0(4)	N(1)–Tc–O(2)	90.5(5)	N(2)–Tc–O(3)	83.4(5)
								O(2)–Tc–O(3)	85.8(5)

(*ii*)

Ligand 1		Ligand 2		Ligand 1		Ligand 2	
O(2)–C(1)	1.33(2)	O(3)–C(14)	1.35(2)	Tc–O(2)–C(1)	125.9(1.1)	Tc–O(3)–C(14)	136.3(1.0)
C(1)–C(2)	1.42(2)	C(14)–C(15)	1.40(2)	O(2)–C(1)–C(2)	113.6(1.5)	O(3)–C(14)–C(15)	118.1(1.6)
C(2)–C(3)	1.38(2)	C(15)–C(16)	1.39(3)	O(2)–C(1)–C(6)	126.6(1.6)	O(3)–C(14)–C(19)	120.9(1.4)
C(3)–C(4)	1.39(3)	C(16)–C(17)	1.39(3)	C(1)–C(2)–C(3)	117.9(1.6)	C(14)–C(15)–C(16)	117.7(1.8)
C(4)–C(5)	1.38(3)	C(17)–C(18)	1.39(3)	C(2)–C(3)–C(4)	122.7(1.8)	C(15)–C(16)–C(17)	121.1(1.8)
C(5)–C(6)	1.39(2)	C(18)–C(19)	1.37(2)	C(3)–C(4)–C(5)	118.2(1.7)	C(16)–C(17)–C(18)	120.3(1.9)
C(6)–C(1)	1.38(2)	C(19)–C(14)	1.42(3)	C(4)–C(5)–C(6)	120.7(1.7)	C(17)–C(18)–C(19)	120.4(1.7)
C(6)–C(7)	1.46(2)	C(19)–C(20)	1.42(2)	C(6)–C(1)–C(2)	119.7(1.6)	C(18)–C(19)–C(14)	119.3(1.6)
C(7)–N(1)	1.29(2)	C(20)–N(2)	1.29(2)	C(1)–C(6)–C(7)	124.6(1.6)	C(19)–C(14)–C(15)	121.0(1.8)
N(1)–C(8)	1.44(2)	N(2)–C(21)	1.46(2)	C(5)–C(6)–C(7)	114.1(1.6)	C(14)–C(19)–C(20)	122.7(1.6)
C(8)–C(9)	1.37(3)	C(21)–C(22)	1.36(3)	C(6)–C(7)–N(1)	125.5(1.5)	C(18)–C(19)–C(20)	118.0(1.6)
C(9)–C(10)	1.38(3)	C(22)–C(23)	1.42(3)	C(7)–N(1)–Tc	123.3(1.1)	C(19)–C(20)–N(2)	127.7(1.7)
C(10)–C(11)	1.37(3)	C(23)–C(24)	1.34(4)	Tc–N(1)–C(8)	121.0(1.0)	C(20)–N(2)–Tc	125.9(1.1)
C(11)–C(12)	1.38(3)	C(24)–C(25)	1.32(4)	C(7)–N(1)–C(8)	115.4(1.3)	Tc–N(2)–C(21)	115.7(1.0)
C(12)–C(13)	1.42(3)	C(25)–C(26)	1.45(4)	N(1)–C(8)–C(9)	119.9(1.5)	C(20)–N(2)–C(21)	118.0(1.4)
C(13)–C(8)	1.45(3)	C(26)–C(21)	1.39(3)	N(1)–C(8)–C(13)	117.0(1.6)	N(2)–C(21)–C(22)	121.5(1.6)
				C(5)–C(6)–C(1)	120.7(1.7)	N(2)–C(21)–C(26)	117.0(1.5)
				C(8)–C(9)–C(10)	118.4(1.7)	C(21)–C(22)–C(23)	118.7(2.0)
				C(9)–C(10)–C(11)	121.2(2.0)	C(22)–C(23)–C(24)	119.2(2.2)
				C(10)–C(11)–C(12)	121.4(2.1)	C(23)–C(24)–C(25)	124.3(2.2)
				C(11)–C(12)–C(13)	120.5(2.0)	C(24)–C(25)–C(26)	118.3(2.1)
				C(12)–C(13)–C(8)	115.4(1.8)	C(25)–C(26)–C(21)	117.9(1.8)
				C(13)–C(8)–C(9)	122.8(1.7)	C(26)–C(21)–C(22)	121.4(1.8)

Table 4. (*a*) Least-squares planes of the form $Px + Qy + Rz = S$, where x,y,z are the fractional co-ordinates

Plane	Atoms	*P*	*Q*	*R*	*S*
1	O(2), N(1), N(2), Cl	8.927	6.489	−7.226	2.372
2	Tc, N(1), N(2)	−8.960	−4.770	7.903	−1.890
3	O(2), N(1), C(1), C(6), C(7)	4.617	8.531	−8.944	2.427
4	O(3), N(2), C(14), C(19), C(20)	4.629	2.070	10.295	3.819
5	C(1)—C(7)	−4.812	−7.786	9.230	−2.141
6	C(8)—C(13)	7.589	−4.045	8.334	0.007
7	C(14)—C(20)	4.423	1.827	10.399	3.787
8	C(21)—C(26)	−3.465	9.182	−8.591	−0.893

(*b*) Distances (Å) of atoms from the planes; atoms included in the least-squares plane are in square brackets

Plane	
1	Tc 0.19, O(1) 1.84, O(3) −1.75 [O(2) −0.01, N(1) 0.01, N(2) −0.01, Cl 0.01]
2	O(1) −1.67, Cl 0.37, O(2) 0.39, O(3) 1.91
3	Tc −0.40, Cl −1.16, O(1) 1.12, O(3) −2.17, N(2) −1.22, C(2) 0.16, C(5) −0.01, C(8) 0.14 [O(2) −0.02, N(1) 0.00, C(1) 0.04, C(6) −0.04, C(7) 0.02]
4	Tc −0.33, Cl 1.99, O(1) −0.91, O(2) −0.44, N(1) −2.33, C(15) −0.03, C(18) −0.02, C(21) −0.03 [O(3) 0.02, N(2) −0.02, C(14) −0.02, C(19) −0.01, C(20) 0.03]
5	Tc 0.36, O(2) 0.08, N(1) −0.09, C(8) −0.31
6	N(1) 0.03, C(7) −1.00
7	Tc −0.41, O(3) 0.00, N(2) −0.08, C(21) −0.11
8	N(2) 0.01, C(20) −0.81

(*c*) Dihedral angles (°) between planes and best lines Tc–O(1) (l^1) and O(3)–Tc–O(1) (l^2)

1—3	22.9	3—6	59.4	2—l^1	2.3
1—4	76.0	4—7	1.4	3—l^1	24.5
2—3	24.7	4—8	43.0	4—l^1	69.9
2—4	71.9	5—6	59.6	1—l^2	2.2
3—4	59.7	6—8	26.4	3—l^2	23.7
3—5	3.1	7—8	42.1	4—l^2	75.1

(*d*) Torsion angles (°)

C(1)–C(6)–C(7)–N(1)	8.8	C(14)–C(19)–C(20)–N(2)	4.8

Table 5. Some important infrared stretching frequencies (cm^{-1}) of technetium and rhenium complexes with the ligands L^1 and L^2

Compound	ν(C=N)	ν(C-O)	ν(M=O)	ν(M-Cl)
$[TcOClL^1_2]$	1 618s, 1 603m	1 310s, 1 285s	940s	320s
$[ReOClL^2_2]$	1 610s, 1 598m	1 296s, 1 280s	959s	310s
$[TcOCl_3L^1]^-$	1 609s, 1 591m	1 305s	951s	318m, 309s, 301m

Table 6. Tc-O bond lengths (Å) in oxides, pertechnetates, TcO^{3+}, and $OTcO^+$ complexes

Compound	C.N.[a]	Oxidation state of Tc	Tc-O	Ref.
Tc_2O_7	4	VII	1.68, 1.84	*b*
$K[TcO_4]$	4	VII	1.71	*c*
$[NH_4][TcO_4]$	4	VII	1.70	*d*
$(TcOF_4)_3$	6	VI	1.66	*e*
$[N(PPh_3)_2][TcOCl_4]$	5	V	1.61	1
$[NBu_4][TcO\{SCH_2C(O)S\}_2]$	5	V	1.67	7
$[AsPh_4][TcO(SCH_2CH_2S)_2]$	5	V	1.64	8
$[Tc(htpzb)Cl_2O]$[f]	6	V	1.66	9
trans-$[Tc(cyclam)O_2][ClO_4]\cdot H_2O$[g]	6	V	1.75	10
$Ba[Tc(O)(edta)]_2$	7	V	1.66	*h*
$[(H_2edta)Tc(O_2)Tc(H_2edta)]\cdot 5H_2O$	7	IV	1.91	*i*
$[TcOClL^1_2]$	6	V	1.67	This work

[a] C.N. = Co-ordination number. [b] B. Krebs, *Angew. Chem.*, 1969, **81**, 328; *Z. Anorg. Allg. Chem.*, 1971, **380**, 146. [c] B. Krebs and K. D. Hasse, *Acta Crystallogr., Sect. B*, 1976, **32**, 1334. [d] B. J. McDonald and G. J. Tyson, *Acta Crystallogr.*, 1962, **15**, 87; R. Faggiani, C. J. Lock, and J. Polè, *Acta. Crystallogr., Sect. B*, 1980, **35**, 231. [e] A. J. Edwards, G. R. Jones, and R. J. C. Sills, *J. Chem. Soc. A*, 1970, 2521. [f] htpzb = Hydridotris(1-pyrazolyl)borate anion. [g] cyclam = 1,4,8,11-Tetra-azacyclotetradecane. [h] E. A. Deutsch, R. C. Elder, and A. Packard, unpublished results. [i] H. B. Bürgi, G. Anderegg, and P. Blaüenstein, *Inorg. Chem.*, 1981, **20**, 3829.

is possible to obtain the bis-ligand complex only by adding an excess of HL^1 in ethanol solution. Also, this compound is air stable in the solid, but the solutions become dark after some hours. Elemental analyses are consistent with the formula $[AsPh_4][TcOCl_3L^1]$. The i.r. spectrum (Table 5) shows the presence of $[AsPh_4]^+$ [ν(C-As) 1 085 cm^{-1}] and the bands of co-ordinated L^1: ν(C=N) at 1 609, 1 591 cm^{-1} and ν(C-O) at 1 305 cm^{-1}; ν(Tc=O) was found at 951 cm^{-1} and ν(Tc-Cl) vibrations are among the bands at 318, 309, and 301 cm^{-1}.

Although the gross structural features could have been predicted, to achieve more structural details a complete *X*-ray analysis of $[TcOClL^1_2]$ (1) was carried out. The structure has several interesting features. Table 6 shows that the TcO^{3+} core may be incorporated (*i*) into five-co-ordinate square-pyramidal complexes (with four chlorine atoms [1] or two bidentate ligands [7,8]), (*ii*) into a six-co-ordinate octahedral complex (with a tripodal tridentate ligand [9]), and (*iii*) into a seven-cordinate pentagonal-bipyramidal complex [with ethylenediaminetetra-acetate (edta) [10]]; this flexible co-ordination environment of the TcO^{3+} core is not surprising when the electronic configuration of Tc^V is considered. In fact, the π-donating ability of the oxo-ligand destabilizes the d_{yz} and d_{xz} orbitals (*z* axis coincident with the Tc-O bond) sufficiently so that the two *d* electrons of Tc^V are paired in the d_{xy} orbital (all the known TcO^{3+} complexes are diamagnetic). Thus the TcO^{3+} core exhibits a ' closed shell ' electronic configuration and does not lose or gain ligand-field stabilization energy as a function of the co-ordination environment. In this situation the d^2 TcO^{3+} core behaves as a d^0 metal and can readily adapt to that co-ordination geometry dictated by the particular properties (denticity, and the number and size of chelate rings) of a given ligand. Moreover, as anticipated by Zuckman *et al.*,[10] the formation of a *trans*-dioxotechnetium(V) species, in the presence of ligand L^1, has to be rejected, since the dioxo-species is formed only if the ligands are merely σ donating or are poor π donors.

In the present complex (1) the technetium centre is in a distorted octahedral environment, the six ligating atoms being one oxygen, one chlorine, and the remainder from the two chelate L^1 ligands (almost mutually orthogonal, one ligand bridging an equatorial and an apical position and the other two equatorial ones, Figure). The structural parameters listed in the Tables are quite normal: *e.g.* Tc-Cl 2.38, Tc-N(1) (*trans* to Cl) 2.12, and Tc-N(2) [*trans* to O(2)] 2.19 Å. The O(2), N(1), N(2), and Cl atoms define an ' equatorial ' plane, with the Tc atom pushed upwards 0.19 Å toward O(1) (oxo-atom). The ' inner core ' is distorted from an ideal octahedral configuration mainly by this movement such that the angles Cl-Tc-N(1) and O(2)-Tc-N(2) are 171.0 and 168.7°, respectively; the O(oxo)-Tc-O(3) angle is also significantly non-linear at 167.1°, while the bond angles in the equatorial plane are rather close to 90°. The O $\cdots$ N ' bite ' of the ligand bridging the equatorial and apical positions (ligand 2) is reduced [2.75 Å; N(2)-Tc-O(3) = 83.4°] when compared with the corresponding values for ligand 1 (2.92 Å and 90.5°). This situation closely parallels that of $[ReOClL^2_2]$,[11] as well as the evidence that O(oxo)-Tc-X(*cis*) is much larger for X = Cl and O (101.1 and 101.9° respectively) than for X = N (87.8 and 89.3°). Moreover, unlike $[ReOClL^2_2]$, the salicylidene ligands are here quite planar (maximum deviation of 0.04 Å) with Tc out of these planes by −0.40 and −0.33 Å. The oxo-ligand is involved in a weak interaction with the hydrogen atom attached to C(9). The O(1) $\cdots$ H(9) distance (located geometrically) is 2.48 Å, the O(1) $\cdots$ H(9) $\cdots$ C(9) angle being 117°. As suggested by several authors,[9,12] the Tc-O(3) bond *trans* to the oxo-ligand should be longer than Tc-O(2) and the *trans* site should be labile. Indeed, while Tc-O(oxo) and Tc-O(2) show ' normal ' values (1.67 and 1.99 Å, respectively) the Tc-O(3) length contracts to 1.94 Å and this feature seems to exclude *trans*-weakening due to the strong π bonding of the oxo-group. This has been noted also in the parent rhenium compound,

$[ReOClL^2_2]$,[11] and the strong π bonding does not produce *trans*-weakening, at least when an RO^- group is found to be *trans* to the Tc–O(oxo) bond.

The synthesis of analogous technetium complexes with more complicated Schiff bases are in progress to determine the different physical and physicochemical properties of the complexes varying the R group in the $HOC_6H_4CH=NR$-*o* moiety. The simplicity of the preparation methods, the short reaction times, the stability of the complexes under normal conditions, and the versatility of the ligands are important in the design of ^{99m}Tc labelled radiopharmaceuticals containing nitrogen- and oxygen-donor atoms.

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