Complexes of Tc^{V} and Tc^{III} with Tridentate Schiff Bases derived from *S*-Methyl Dithiocarbazate. Crystal Structures of Chloro[*S*-methyl 3-(2′-hydroxy-1-naphthylmethylene)dithiocarbazato(2-)]oxotechnetium(V) and Dichloro[*S*-methyl 3-(2-hydroxybenzylidene)dithiocarbazato(1-)]bis(triphenylphosphine)-technetium(III)†

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New square-pyramidal oxotechnetium(V) complexes of the type [TcO(Cl)(L)], and octahedral technetium(III) complexes of the type $[TcCl_2(HL)(PPh_3)_2]$, where L and HL indicate respectively the dianionic tridentate and the monoanionic bidentate forms of a Schiff-base ligand derived from the methyl ester of dithiocarbazic acid, have been synthesized and characterized. The crystal structures of the compounds $[TcO(Cl)(L^6)]$ [H_2L^6 = *S*-methyl 3-(2′-hydroxy-1′-naphthylmethylene)-dithiocarbazate] and $[TcCl_2(HL^1)(PPh_3)_2]\cdot CH_2Cl_2$ [H_2L^1 = *S*-methyl 3-(2′- hydroxybenzylidene)-dithiocarbazate] have been determined.

The recent application in diagnostic nuclear medicine of the lipophilic complex [^{99m}TcO(L)] (L = 3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate as a cerebral blood flow imaging agent[1] has stimulated the search for other lipophilic technetium complexes having a higher degree of localization in the cerebral region. The above complex was found to possess a square-pyramidal geometry, with the $[Tc{=}O]^{3+}$ group in an apical position and the quadridentate trianionic ligand spanning the four positions in the plane normal to it.[2] This fact, and the closely related observation that other lipid-soluble square-pyramidal oxo-technetium(V) complexes with diaminodithiolates cross the blood–brain barrier,[3] seem to indicate that the formation of a square-pyramidal structure with an apical TcX group, where X represents a multiply bonded donor atom, is a favourable feature (although not sufficient) for obtaining a ^{99m}Tc-containing radiopharmaceutical which may function as a useful regional cerebral blood flow imaging agent.

Recently, we reported the synthesis of a new class of square-pyramidal nitridotechnetium(V) complexes of the type [TcN(L)-(PPh_3)] and [TcN(L′)$_2$], where L and L′ were respectively a tri- or bi-dentate Schiff-base ligand derived from *S*-methyl dithiocarbazate $NH_2NHC(=S)SCH_3$.[4] The present work extends our investigations to the synthesis of analogous square-pyramidal technetium(V) complexes having a $[Tc{=}O]^{3+}$ group in place of the isoelectronic $[Tc{\equiv}N]^{2+}$ group, in order to compare their properties and stabilities with those of the corresponding nitrido complexes. Owing to our interest in square-pyramidal structures, we utilized only tridentate Schiff-base derivatives of *S*-methyl dithiocarbazate of the type shown below. It is known that bi- and quadri-dentate Schiff bases having respectively N,O^- or N,S^- and O^-,N,N,O^- or S^-,N,N,S^- as donor sets give rise to quasi-octahedral oxotechnetium(V) complexes, while analogous tridentate O^-,N,O^- or O^-,N,S^- Schiff bases prefer to bind the $[Tc{=}O]^{3+}$ group in a square-pyramidal geometry.[5]

When this work was in preparation, a series of papers appeared on the synthesis of oxotechnetium(V) complexes with bidentate N,S^- and quadridentate S^-,N,N,S^- Schiff bases derived from S-methyl dithiocarbazate.[6] It was found that, as expected, the complexes possess a pseudo-octahedral geometry with the ligands co-ordinated in the plane normal to the Tc=O bond.

We report here the synthesis and characterization of new square-pyramidal oxotechnetium(V) complexes with the ligands illustrated, and the crystal-structure determination of the complex $[TcO(Cl)(L^6)]$ [H_2L^6 = *S*-methyl 3-(2′-hydroxy-1′-naphthylmethylene)dithiocarbazate]. We will also discuss the reactivity of these new complexes towards triphenylphosphine and report the crystal structure of the reduced technetium(III) complex $[TcCl_2(HL^1)(PPh_3)_2]$ [H_2L^1 = *S*-methyl 3-(2′-hydroxybenzylidene)dithiocarbazate].

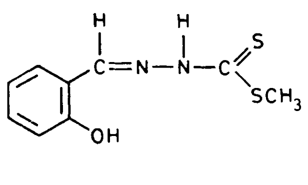
Experimental

General.—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 years. When this material is handled in milligram amounts it does not present a serious hazard since common laboratory equipment provides adequate shielding. 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.

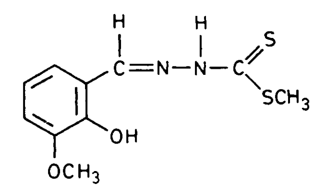
All common laboratory chemicals were reagent grade. Technetium, as $[NH_4][TcO_4]$ in 0.1 mol dm^{-3} ammonia solutions, was purchased from the Radiochemical Centre, Amersham, England. The compounds $[AsPh_4][TcOCl_4]$, $[NBu^n{}_4]$-$[TcOCl_4]$, and $[TcCl_4(PPh_3)_2]$ were prepared as reported previously.[7] The Schiff bases H_2L^n (n = 1—7) were prepared by literature methods.[8]

I.r. spectra were recorded on a Perkin-Elmer 599 grating spectrometer using KBr pellets or Nujol mulls between CsI

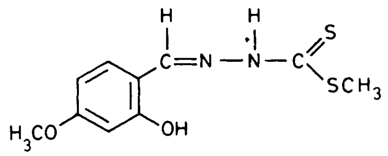
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



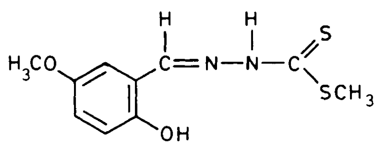
H_2L^1



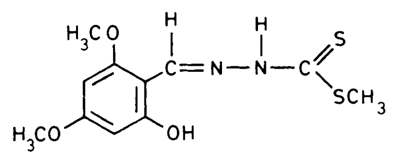
H_2L^2



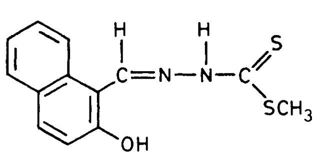
H_2L^3



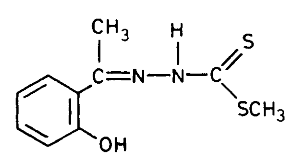
H_2L^4



H_2L^5



H_2L^6



H_2L^7

disks. Proton n.m.r. spectra in $CDCl_3$ solutions were recorded on a Varian 300-MHz Gemini spectrometer. Magnetic susceptibility measurements were carried out by Evans method[9] on the same apparatus. Elemental analyses were performed on a model 1106 Carlo Erba elemental analyzer; the analyses for the radioactive technetium compounds were carried out on a Packard liquid-scintillation instrument, model TRI-CARB 300 C, with Insta-gel as scintillator, after dissolution of the samples in hydrogen peroxide–nitric acid solutions.

Synthesis of the Complexes.—$[TcO(Cl)(L^n)]$ (n = 1—7). The $[NBu^n{}_4]^+$ or $[AsPh_4]^+$ salts of $[TcOCl_4]^-$ (0.150 mmol) were treated with a two-fold molar excess of the relevant ligand in ethanol (10 cm^3), at room temperature, with stirring. The solution immediately became dark red, and, after a few minutes, a red powder formed, which was collected by filtration and washed with EtOH and pentane. Recrystallization was from CH_2Cl_2–EtOH. Yield 80%.

The complex $[TcO(Cl)(L^7)]$ was also prepared using the procedure in ref. 10, and the product recovered shown to be identical to that obtained by the method described above (see Results and Discussion sections).

$[TcCl_2(HL^n)(PPh_3)_2]$ (n = 1 or 6). To an ethanolic solution (40 cm^3) of the $[NBu^n{}_4]^+$ or $[AsPh_4]^+$ salts of $[TcOCl_4]^-$ (0.300 mmol), HCl (1 cm^3, 12 mol dm^{-3}), H_2L^n (0.400 mmol), and triphenylphosphine (1.200 mmol) were added at room temperature, and the mixture was refluxed for 1 h under an argon stream. A brown powder precipitated, which was filtered off and washed with hot EtOH (5 cm^3) and pentane. Recrystallization from CH_2Cl_2–EtOH gave dark red crystals of the final compound. Yield 26%.

It is remarkable that no reduction was observed on treating the complexes $[TcOCl(L^n)]$ (n = 1 or 6) with PPh_3 in boiling EtOH. No reactivity was also observed in the reaction of the complex $[TcCl_4(PPh_3)_2]$ with an excess of the relevant Schiff base (H_2L^n, n = 1—7), in boiling toluene.

Crystal Structure Determinations for $[TcO(Cl)(L^6)]$ **(1)** *and* $[TcCl_2(HL^1)(PPh_3)_2]$ **(2)**.—Crystals of complexes **(1)** and **(2)** were obtained as described in the corresponding syntheses.

Crystal data. **(1)** $C_{13}H_{10}ClN_2O_2S_2Tc$, $M = 424.8$, orthorhombic, $a = 7.102(3)$, $b = 14.697(5)$, $c = 14.732(4)$ Å, $U = 1\,537.7(9)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_12_12_1$, $Z = 4$, $D_c = 1.83$ g cm^{-3}, $\mu = 13.54$ cm^{-1}, crystal dimensions 0.06 × 0.18 × 0.40 mm.

(2) $C_{45}H_{39}Cl_2N_2OP_2S_2Tc{\cdot}CH_2Cl_2$, $M = 1004.7$, monoclinic, $a = 14.504(6)$, $b = 16.281(8)$, $c = 19.752(11)$ Å, $\beta = 96.78(4)°$, $U = 4\,632(4)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group $P2_1/n$ (alternative $P2_1/c$, no. 14), $Z = 4$, $D_c = 1.44$ g cm^{-3}, $\mu = 7.25$ cm^{-1}, crystal dimensions 0.08 × 0.12 × 0.36 mm.

Data collection and processing. CAD4 diffractometer, ω—2θ mode, graphite-monochromated Mo-K_α radiation: **(1)** 2 544 unique reflections measured ($2 \leqslant \theta \leqslant 30°$), giving 1 580 with $I \geqslant 2\sigma(I)$, corrected for absorption (minimum transmission factor = 0.725); **(2)** 8 151 unique reflections measured ($2 \leqslant \theta \leqslant 25°$), giving only 1 169 with $I \geqslant 3\sigma(I)$, corrected for absorption (minimum transmission factor = 0.91).

Structure analysis and refinement. Solution by Patterson and Fourier methods. For complex **(1)**, full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. The weighting scheme $w = 4F_o{}^2/[\sigma^2(F_o{}^2) + (0.05F_o{}^2)^2]$ gave satisfactory agreement analyses. For **(2)** the solvent molecule CH_2Cl_2 was found to be disordered. Full-matrix least squares with anisotropic thermal parameters for Tc, Cl(1), Cl(2), P(1), P(2), S(1), S(2), O(1), and N(1) and isotropic ones for all the other non-H atoms; hydrogens in calculated positions with the exception of the hydrogen bonded to O(1) atom whose position remains undetermined. The weighting scheme $w = 4F_o{}^2/[\sigma^2(F_o{}^2) + (0.08F_o{}^2)^2]$ gave satisfactory agreement analyses. Final R and R' values are 0.051 and 0.054 for **(1)**, 0.076 and 0.088 for **(2)**. Programs used and sources of scattering-factor data are given in ref. 11.

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

Results

The complexes $[TcO(Cl)(L^n)]$ (H_2L^n, n = 1—7) were prepared, at room temperature, in EtOH, by mixing $[TcOCl_4]^-$ with an excess of the appropriate ligand. When the same reaction was carried out in the presence of an excess of HCl and triphenylphosphine the product $[TcCl_2(HL^n)(PPh_3)_2]$ was obtained, in which technetium has been reduced to the +3 oxidation state.

Table 1. Physical properties of the oxotechnetium complexes

Complex	Analysis* (%) C	H	N	S	Tc	Yield(%)	$\mu_{eff.}$
[TcO(Cl)(L[1])]	29.1 (28.8)	2.2 (2.1)	7.2 (7.4)	17.1 (17.0)	27.8 (26.4)	85	Diamagnetic
[TcO(Cl)(L[2])]	30.1 (29.7)	2.6 (2.5)	6.7 (6.9)	15.0 (15.8)	25.1 (24.5)	78	Diamagnetic
[TcO(Cl)(L[3])]	30.4 (29.7)	2.7 (2.5)	6.6 (6.9)	14.8 (15.8)	24.9 (24.5)	76	Diamagnetic
[TcO(Cl)(L[4])]	30.6 (29.7)	2.7 (2.5)	6.5 (6.9)	15.0 (15.8)	24.7 (24.5)	78	Diamagnetic
[TcO(Cl)(L[5])]	29.9 (30.5)	2.5 (2.3)	6.3 (6.5)	14.5 (14.8)	24.0 (22.8)	75	Diamagnetic
[TcO(Cl)(L[6])]	36.1 (36.7)	2.2 (2.4)	6.3 (6.6)	14.9 (15.1)	23.1 (23.3)	88	Diamagnetic
[TcO(Cl)(L[7])]	30.2 (30.9)	2.8 (2.6)	7.1 (7.2)	16.0 (16.5)	25.2 (25.5)	83	Diamagnetic
$[TcCl_2(HL^1)(PPh_3)_2]$	59.1 (58.8)	4.4 (4.3)	3.4 (3.1)	6.8 (7.0)	11.0 (10.8)	28	2.45
$[TcCl_2(HL^6)(PPh_3)_2]$	61.1 (60.8)	4.6 (4.3)	3.2 (2.9)	6.8 (6.6)	10.5 (10.2)	24	2.43

* Calculated values in parentheses.

Table 2. I.r. and ^{1}H n.m.r. data for the oxotechnetium complexes

Complex	I.r.(cm^{-1})[a] ν(C=N)	ν(Tc=O)	ν(Tc–S)	^{1}H N.m.r.[b]
[TcO(Cl)(L[1])]	1 600	985	370	2.8(s)(SCH_3)
[TcO(Cl)(L[2])]	1 600	980	370	2.8(s)(SCH_3) 4.0(s)(OCH_3)
[TcO(Cl)(L[3])]	1 610	970	365	2.8(s)(SCH_3) 3.9(s)(OCH_3)
[TcO(Cl)(L[4])]	1 610	975	375	2.8(s)(SCH_3) 3.8(s)(OCH_3)
[TcO(Cl)(L[5])]	1 610	980	365	2.8(s)(SCH_3) 4.0(s)(OCH_3) 4.1(s)(OCH_3)
[TcO(Cl)(L[6])]	1 615	980	360	2.8(s)(SCH_3)
[TcO(Cl)(L[7])]	1 595	980	365	2.8(s)(SCH_3) 3.4(s)(CCH_3)
$[TcCl_2(HL^1)(PPh_3)_2]$[c]	1 590			
$[TcCl_2(HL^6)(PPh_3)_2]$[d]	1 600			

[a] KBr spectra. [b] Relative to $SiMe_4$ in $CDCl_3$ solution. [c] ν(Tc–Cl) 315, ν(O–H) 3 050, and ν(Tc–P) 1 090 cm^{-1}. [d] ν(Tc–Cl) 320, ν(O–H) 3 080, and ν(Tc–P) 1 090 cm^{-1}.

Such a reduction reaction was conducted only with the ligands H_2L^1 and H_2L^6.

It is interesting that the square-pyramidal complexes [TcO(Cl)(L^n)] (n = 1—7) did not react, in refluxing EtOH, with PPh_3 to produce compounds in which technetium was in a lower oxidation state, indicating that they are not intermediates in the formation of the complexes $[TcCl_2(HL^n)(PPh_3)_2]$ from $[TcOCl_4]^-$.

The complexes were characterized by elemental analysis, i.r. and ^{1}H n.m.r. spectra, and magnetic susceptibility measurements in solution. Details are given in Tables 1 and 2.

The oxotechnetium(v) complexes [TcO(Cl)(L^n)] (n = 1—7) are diamagnetic in solution, consistent with the existence of a closed-shell $Tc=O^{3+}$ core;[12] the existence of this group is also supported by the presence, in the i.r. spectra, of a strong band in the region 970—985 cm^{-1} characteristic of a Tc=O multiple bond.[13] No absorptions attributable with certainty to a ν(Tc–Cl) stretching frequency were observed in the 200—350 cm^{-1} region, characteristic for the technetium–chlorine bond vibration, and this probably indicates that these transitions are of low intensity.

The complexes $[TcCl_2(HL^n)(PPh_3)_2]$ (n = 1 or 6) are paramagnetic in solution, with magnetic moments consistent with two unpaired electrons and with a +3 oxidation state for technetium.[14] No assignments of ^{1}H n.m.r. signals were made for these complexes, owing to the line broadening caused by their paramagnetism.[14]

Discussion

The data on the characterization of the complexes [TcO(Cl)(L^n)] (n = 1—7) (Tables 1 and 2), together with the crystal-structure determination of one member of this class, [TcO(Cl)(L[6])] (see below), indicate that they are square pyramidal with the Tc=O group in an apical position; the tridentate dianionic L^n ligand spans three positions in the plane normal to the Tc=O through the neutral β-nitrogen atom, the charged phenolic oxygen atom, and the charged thiol sulphur atom, the fourth site on that plane being occupied by a chlorine atom. Thus, the structure and properties of these complexes do not differ substantially from those described for other square-pyramidal oxotechnetium(v) complexes with tridentate Schiff bases.[15]

In a recent report[10] the synthesis and characterization of a paramagnetic isomer of the diamagnetic square-pyramidal complex [TcO(Cl)(L[7])], discussed here, were described; in order to account for its anomalous magnetic behaviour, a trigonal-bipyramidal geometry was suggested. These observations led us to consider the existence of two isomers of the complex [TcO(Cl)(L[7])], having a square-pyramidal and a trigonal-bipyramidal geometry respectively, and forming the first example of isomerism observed in oxotechnetium(v) chemistry. We tried, therefore, to obtain the paramagnetic isomer by following exactly the same procedure described in the literature, but we isolated invariably the diamagnetic complex, a fact that remains unexplained.

Only small differences in the values of the ν(Tc=O) and ν(C=N) frequencies have been observed between the square-pyramidal complex prepared here, and the supposed trigonal-bipyramidal isomer [ν(Tc=O) 980 and 985, ν(C=N) 1 595 and

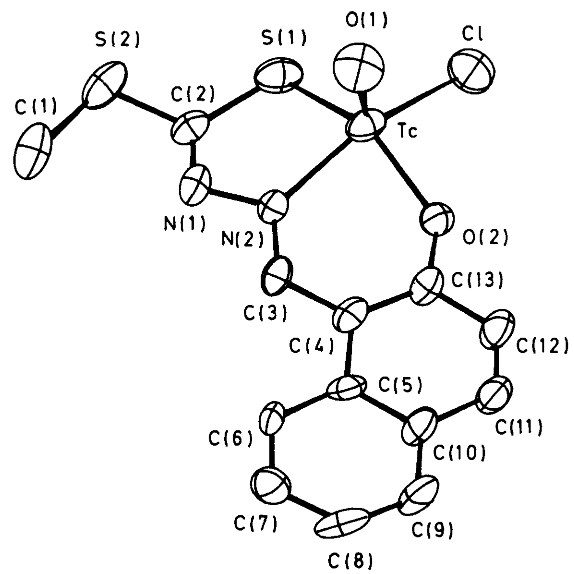


Figure 1. A view of complex (1) showing the thermal ellipsoids at 40% probability, drawn using ORTEP (C. K. Johnson, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976)

Table 3. Positional parameters ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for compound (1)

Atom	*x*	*y*	*z*
Tc	2 016(1)	415.6(5)	−1 496.3(5)
Cl	862(4)	1 141(2)	−214(2)
S(1)	−974(4)	36(2)	−1 840(2)
S(2)	−2 260(4)	−1 015(2)	−3 398(2)
O(1)	3 124(11)	−497(5)	−1 129(4)
O(2)	3 524(10)	1 529(4)	−1 610(4)
N(1)	965(10)	−176(5)	−3 373(5)
N(2)	2 284(9)	335(5)	−2 863(4)
C(1)	−1 231(16)	−1 330(8)	−4 476(8)
C(2)	−532(12)	−361(6)	−2 957(6)
C(3)	3 631(12)	669(6)	−3 356(5)
C(4)	5 057(12)	1 273(5)	−3 043(6)
C(5)	6 644(12)	1 475(5)	−3 622(5)
C(6)	6 954(14)	1 089(5)	−4 464(5)
C(7)	8 497(13)	1 287(6)	−4 985(6)
C(8)	9 817(15)	1 899(6)	−4 677(7)
C(9)	9 610(14)	2 332(6)	−3 837(7)
C(10)	8 011(14)	2 117(5)	−3 313(6)
C(11)	7 728(15)	2 537(6)	−2 442(6)
C(12)	6 229(16)	2 340(6)	−1 921(7)
C(13)	4 898(13)	1 679(6)	−2 190(6)

1 600 cm^{-1} respectively], however, a remarkable difference has been found in the ν(Tc–S) frequency, which falls at 365 cm^{-1} for the square-pyramidal complex and at 300 cm^{-1} for the trigonal-bipyramidal isomer.[10] We consider that all these results together still contribute to keep the existence of the latter isomer an open question.

The *X*-ray analysis of the complex [$TcCl_2(HL^1)(PPh_3)_2$] (see below) shows that it has an octahedral structure with the two PPh_3 groups in *trans* position to each other, and the two chlorine atoms in *cis* position, L^1 being co-ordinated to the metal as a bidentate monoanionic ligand through the neutral α-nitrogen atom and the charged thiol sulphur atom, the phenolic oxygen atom remaining protonated. The analogous complex [$TcCl_2(HL^6)(PPh_3)_2$] possesses similar spectroscopic and magnetic properties, so that the same structure can be attributed to it.

The technetium(III) complexes cannot be prepared by reduction of [$TcO(Cl)(L^n)$] (n = 1—7) with PPh_3. This lack of reactivity of square-pyramidal oxotechnetium(V) complexes towards reducing phosphines has been already noted, and compared with the behaviour of octahedral oxotechnetium(V) complexes, which, on the contrary, are easily reduced by tertiary phosphines to give technetium(III) complexes.[14] This fact may be attributed to the existence of a weaker Tc=O multiple bond in octahedral structures than in square-pyramidal ones; this weakening increases on increasing the basicity of the ligand *trans* to the Tc=O group.[5]

Description of the Structures.—[$TcO(Cl)(L^6)$] (**1**). The monomeric unit consists of a square-pyramidal complex of Tc^V, with the oxo-oxygen atom in an apical position, the tridentate O^-,N,S^- ligand, and a chlorine atom *trans* to N(2) forming the basal plane (Figure 1). The spatial arrangement of the atoms around the Tc atom is similar to that found in the previously reported structure of the analogous nitridotechnetium(V) complex [$TcN(L^1)(PPh_3)$];[4] the Tc atom is displaced by 0.693(1) Å from the plane defined by N(2), S(1), O, and Cl, pointing towards the O_{oxo} atom. The naphthyl moiety of the ligand is nearly planar, the angle between the least-squares planes P1[C(5)—C(10), $\Sigma(\Delta/\sigma)^2$ = 1.5] and P2[C(4)—C(13), $\Sigma(\Delta/\sigma)^2$ = 17.6] being 1.4(2)°. The C(4)—C(13) ring forms an angle of 17.0(2)° with the plane defined by N(2), C(3), C(4), O(2), and Tc, and an angle of 25.1(2)° with that defined by N(2), N(1), C(2), S(1), and Tc.

The Tc=O_{oxo} distance is 1.645(7) Å, indicating strong multiple-bond character. This distance is remarkably longer than the Tc≡N bond distance found in the compound [$TcN(L^1)(PPh_3)$],[4] in accord with the fact that the nitrido group is a 'harder' base than the O_{oxo} group. Conversely, a lengthening of the apical bond corresponds to a strengthening of the basal distances, which are shorter in the oxo-complex by 0.079, 0.091, and 0.099 Å for the Tc–N, Tc–O, and Tc–S bonds respectively.

The labilization of the basal bonds in square-pyramidal nitridotechnetium(V) complexes is a general phenomenon: for instance, a similar lengthening has been found in the complex [$TcN(S_2N_2C_5H_9)_2$] (+0.135 and +0.091 Å for Tc–N and Tc–S respectively).[16] This fact can be understood on the basis that the oxo ligand is less effective at neutralizing the charge of the technetium(V) centre than is the N^{3-} ligand, and therefore the basal ligands will be drawn more closely to the metal in an oxo complex than in a nitrido complex, in line with simple electrostatic considerations.

All other bond distances are normal and do not require further discussions. The molecules are packed without significant intra- or inter-molecular short contacts.

[$TcCl_2(HL^1)(PPh_3)_2$] (**2**). The asymmetric unit consists of an octahedral complex of Tc^{III} and of a disordered CH_2Cl_2 solvent molecule, which has been omitted in the view of the molecule in Figure 2 [the isotropic thermal parameters, B(Å^2), are 18(3) for the C atom and 22(1) for the two Cl atoms in the CH_2Cl_2 molecule]. The poor quality and the small size of the crystal, together with the disorder in the unit cell, did not allow a good refinement of the structure from the intensity data, as revealed by the high standard deviations of the structural parameters.

The Tc^{III} is octahedrally co-ordinated to two Cl atoms, two PPh_3 groups, and to N(2) and S(1) atoms of the Schiff base, which acts as a bidentate ligand. Atoms Cl(1) and Cl(2) are *trans* to S(1) and N(2) respectively, and these four atoms form the equatorial plane of the octahedron. Analysis of the angles shows that this plane is not a regular square: the S(1)–Tc–N(2) angle is markedly less than Cl(1)–Tc–Cl(2), Cl(1)–Tc–N(2), and

Table 4. Positional parameters (× 10^4) with e.s.d.s in parentheses for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Tc	1 174(2)	2 176(2)	−1 808(2)	C(20)	4 670(28)	2 651(27)	219(20)*
Cl(1)	1 273(7)	2 571(5)	−2 953(5)	C(21)	4 148(27)	2 896(28)	−385(20)*
Cl(2)	1 916(6)	890(6)	−1 847(5)	C(22)	3 498(22)	2 844(24)	−2 068(16)*
P(1)	2 676(7)	2 872(7)	−1 435(5)	C(23)	3 592(27)	2 291(27)	−2 519(20)*
P(2)	− 334(7)	1 491(6)	−2 149(5)	C(24)	4 235(26)	2 325(26)	−2 938(19)*
S(1)	873(7)	2 162(7)	−628(5)	C(25)	4 813(25)	2 967(24)	−2 961(19)*
S(2)	−137(8)	3 774(8)	−353(6)	C(26)	4 714(29)	3 585(27)	−2 569(21)*
O	−1 038(19)	5 225(18)	−1 694(14)	C(27)	4 095(27)	3 537(25)	−2 085(20)*
N(1)	33(19)	3 946(18)	−1 753(14)	C(28)	−421(24)	869(22)	−2 945(18)*
N(2)	487(20)	3 232(17)	−1 529(15)*	C(29)	258(26)	740(23)	−3 355(19)*
C(1)	204(30)	3 298(28)	461(22)*	C(30)	125(25)	282(23)	−3 920(19)*
C(2)	399(24)	3 096(21)	−880(19)*	C(31)	−765(27)	−29(23)	−4 141(20)*
C(3)	132(28)	4 195(25)	−2 310(21)*	C(32)	−1 473(28)	110(26)	−3 773(21)*
C(4)	−215(31)	4 911(27)	−2 609(23)*	C(33)	−1 330(26)	578(23)	−3 183(20)*
C(5)	−75(34)	5 181(30)	−3 191(24)*	C(34)	−727(23)	760(21)	−1 529(18)*
C(6)	−376(33)	5 904(30)	−3 621(25)*	C(35)	−1 624(25)	635(24)	−1 455(19)*
C(7)	−919(27)	6 394(25)	−3 263(20)*	C(36)	−1 968(27)	69(24)	−1 075(20)*
C(8)	−1 173(28)	6 166(26)	−2 601(21)*	C(37)	−1 359(28)	−427(26)	−705(20)*
C(9)	−786(28)	5 429(26)	−2 302(21)*	C(38)	−409(32)	−375(28)	−748(24)*
C(10)	2 476(21)	3 908(20)	−1 195(16)*	C(39)	−66(23)	174(20)	−1 208(17)*
C(11)	2 339(23)	4 496(20)	−1 695(17)*	C(40)	−1 216(23)	2 291(23)	−2 321(17)*
C(12)	2 171(27)	5 338(25)	−1 559(20)*	C(41)	−1 498(27)	2 542(24)	−2 976(20)*
C(13)	2 071(30)	5 507(28)	−944(22)*	C(42)	−2 178(31)	3 192(27)	−3 054(24)*
C(14)	2 104(30)	4 976(26)	−402(21)*	C(43)	−2 458(29)	3 516(26)	−2 520(21)*
C(15)	2 358(22)	4 150(21)	−566(16)*	C(44)	−2 300(29)	3 235(26)	−1 883(21)*
C(16)	3 415(22)	2 454(19)	−668(16)*	C(45)	−1 569(24)	2 550(21)	−1 759(18)*
C(17)	3 246(22)	1 704(21)	−423(17)*	Cl(1′)	2 877(18)	2 917(18)	5 180(14)*
C(18)	3 826(30)	1 396(27)	162(23)*	Cl(2′)	1 959(19)	4 243(17)	5 620(14)*
C(19)	4 517(24)	1 906(22)	445(18)*	C(1′)	2 774(55)	3 626(49)	5 861(41)*

* Refined isotropically.

Table 5. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for compound (**1**)

Tc–Cl	2.319(3)	S(2)–C(2)	1.690(8)
Tc–S(1)	2.253(3)	O(2)–C(13)	1.319(10)
Tc–O(1)	1.645(7)	N(1)–N(2)	1.414(10)
Tc–O(2)	1.961(6)	N(1)–C(2)	1.259(10)
Tc–N(2)	2.026(6)	N(2)–C(3)	1.297(10)
S(1)–C(2)	1.774(9)	C(3)–C(4)	1.426(11)
S(2)–C(1)	1.809(13)		
Cl–Tc–S(1)	87.9(1)	C(1)–S(2)–C(2)	100.9(5)
Cl–Tc–O(1)	106.0(2)	Tc–O(2)–C(13)	126.8(5)
Cl–Tc–O(2)	83.0(2)	N(2)–N(1)–C(2)	114.5(7)
Cl–Tc–N(2)	150.4(2)	Tc–N(2)–N(1)	119.8(5)
S(1)–Tc–O(1)	108.7(3)	Tc–N(2)–C(3)	127.1(5)
S(1)–Tc–O(2)	134.5(2)	N(1)–N(2)–C(3)	113.0(6)
S(1)–Tc–N(2)	81.4(2)	S(1)–C(2)–S(2)	114.5(5)
O(1)–Tc–O(2)	116.7(3)	S(1)–C(2)–N(1)	122.1(7)
O(1)–Tc–N(2)	103.6(3)	S(2)–C(2)–N(1)	123.4(7)
O(2)–Tc–N(2)	85.0(3)	N(2)–C(3)–C(4)	125.4(7)
Tc–S(1)–C(2)	97.0(3)		

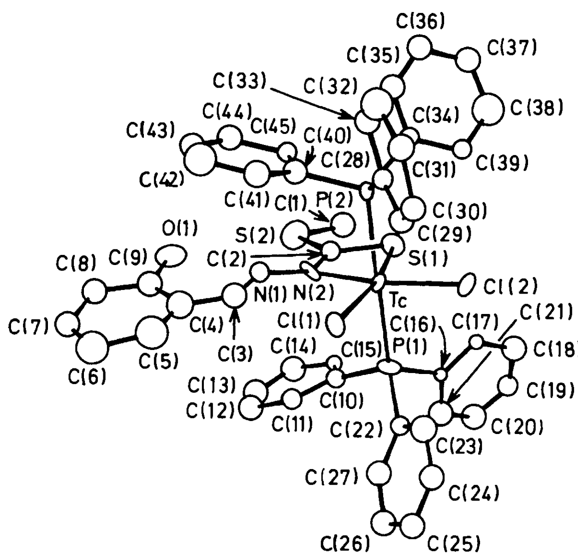


Figure 2. An ORTEP view of complex (**2**) showing the thermal ellipsoids at 40% probability

Cl(2)–Tc–S(1), because of the small bite of the bidentate ligand. The angles of the octahedron involving P atoms are more regular and in the range 88—92°.

The Tc^{III}–N(2) distance does not differ from the Tc–N distances found in compound (**1**), while there is a lengthening in the Tc–S and Tc–Cl distances. A simple hard–soft acid–base scheme may account for this behaviour;[17] the decrease in the oxidation number from +5 to +3 turns the Tc atom into a softer acid forming weaker bonds with the hard S^- and O^- bases. The same phenomenon occurs with rhenium complexes in different oxidation states.[17]

A short intramolecular contact of 2.61(4) Å between N(1) and O atoms indicates the probable presence of hydrogen bonding. No intramolecular contacts shorter than the sum of the van der Waals radii have been found.

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Table 6. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for compound (**2**)

Tc–Cl(1)	2.37(1)	S(2)–C(1)	1.80(4)
Tc–Cl(2)	2.36(1)	S(2)–C(2)	1.76(4)
Tc–P(1)	2.49(1)	O–C(9)	1.34(5)
Tc–P(2)	2.48(1)	N(1)–N(2)	1.38(4)
Tc–S(1)	2.42(1)	N(1)–C(3)	1.20(5)
Tc–N(2)	2.09(3)	N(2)–C(2)	1.32(5)
P(1)–C(10)	1.78(3)	C(3)–C(4)	1.38(6)
P(1)–C(16)	1.88(3)	C(4)–C(5)	1.27(7)
P(1)–C(22)	1.83(4)	C(4)–C(9)	1.37(6)
P(2)–C(28)	1.86(4)	C(5)–C(6)	1.49(7)
P(2)–C(34)	1.84(4)	C(6)–C(7)	1.37(6)
P(2)–C(40)	1.83(4)	C(7)–C(8)	1.45(6)
S(1)–C(2)	1.72(4)	C(8)–C(9)	1.42(6)
Cl(1)–Tc–Cl(2)	97.5(4)	C(16)–P(1)–C(22)	100.8(15)
Cl(1)–Tc–P(1)	90.5(4)	Tc–P(2)–C(28)	116.4(12)
Cl(1)–Tc–P(2)	90.8(4)	Tc–P(2)–C(34)	116.2(12)
Cl(1)–Tc–S(1)	163.4(4)	Tc–P(2)–C(40)	107.8(12)
Cl(1)–Tc–N(2)	96.5(8)	C(28)–P(2)–C(34)	102.4(16)
Cl(2)–Tc–P(1)	91.6(4)	C(28)–P(2)–C(40)	104.7(16)
Cl(2)–Tc–P(2)	89.0(3)	C(34)–P(2)–C(40)	108.6(16)
Cl(2)–Tc–S(1)	99.1(4)	Tc–S(1)–C(2)	79.9(13)
Cl(2)–Tc–N(2)	166.0(9)	C(1)–S(2)–C(2)	99.4(20)
P(1)–Tc–P(2)	178.5(4)	N(2)–N(1)–C(3)	118.3(32)
P(1)–Tc–S(1)	88.3(4)	Tc–N(2)–N(1)	146.1(22)
P(1)–Tc–N(2)	88.6(8)	Tc–N(2)–C(2)	102.8(22)
P(2)–Tc–S(1)	90.2(4)	N(1)–N(2)–C(2)	110.8(28)
P(2)–Tc–N(2)	90.5(8)	S(1)–C(2)–S(2)	125.0(22)
S(1)–Tc–N(2)	67.0(8)	S(1)–C(2)–N(2)	110.4(25)
Tc–P(1)–C(10)	110.2(11)	S(2)–C(2)–N(2)	124.6(27)
Tc–P(1)–C(16)	118.0(11)	N(2)–C(3)–C(4)	127.2(40)
Tc–P(1)–C(22)	113.9(11)	C(3)–C(4)–C(9)	122.7(41)
C(10)–P(1)–C(16)	102.9(15)	O–C(9)–C(4)	119.2(38)
C(10)–P(1)–C(22)	110.2(16)		

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