Synthesis and Characterization of Technetium-(IV) and -(III) Complexes with Bidentate Schiff Bases.† *X*-Ray Molecular Structure of Chloro(dimethylphenylphosphine)bis(*N*-phenylsalicylideneiminato)technetium(III)

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The complexes [$TcCl_4(HL)_2$] and [$TcCl_3L(PPh_3)$] [HL = *N*-methylsalicylideneimine or *N*-phenylsalicylideneimine (Hpsal)] of the long-lived isotope technetium-99 were synthesized from [$TcCl_4(PPh_3)_2$], while the complexes [$TcClL_2(PMe_2Ph)$] were obtained through the reduction of the oxotechnetium(V) complexes [$TcO(Cl)L_2$] with PMe_2Ph. The crystal structure of the complex [$TcCl(psal)_2(PMe_2Ph)$] has been determined: *a* = 9.500(4), *b* = 10.596(4), *c* = 31.000(9) Å, β = 95.59(5)°, monoclinic, space group $P2_1/c$, and *Z* = 4. The co-ordination around Tc is approximately octahedral with the two chelate ligands mutually orthogonal, one ligand bridging two adjacent positions in the plane normal to the Tc–P bond and the other in the plane normal to the Tc–Cl bond. The phosphorus atom of PMe_2Ph is in a position *trans* to the aldimine nitrogen of one of the psal ligands, while the chlorine atom is *trans* to the nitrogen atom of the second psal, leaving the two phenolic oxygens in *trans* positions to each other.

Studies of the inorganic chemistry of technetium are currently of importance in supporting the design of new ^{99m}Tc radiopharmaceuticals having a potential use in nuclear medicine.

A large number of ligands have been used in attempts to stabilize lower oxidation states of this metal. Polydentate Schiff-base ligands possess good co-ordination properties toward technetium cores such as TcO^{3+}, TcO_2^+, or $(\mu\text{-}O)Tc_2O_2^{4+}$, and can be thought to act as stabilizing groups for a variety of metal oxidation states. Schiff-base complexes of technetium have been extensively studied, mainly in reactions involving the Tc^{5+} centre.[1–6] Only a few compounds with quadridentate Schiff bases and containing the technetium ion in oxidation states lower than +5 have been reported.[7]

This paper deals with the synthesis of complexes of Tc^{IV} and Tc^{III} with bidentate Schiff bases: (*i*) by substitution reactions of halogenophosphinetechnetium(IV) complexes, and (*ii*) through the reduction of oxotechnetium(V)–Schiff base compounds with PMe_2Ph to give the corresponding technetium(III) complexes. The products isolated, [$TcCl_3L(PPh_3)$], [$TcCl_4(HL)_2$], and [$TcClL_2(PMe_2Ph)$] [HL = *N*-methylsalicylideneimine (Hmsal) or *N*-phenylsalicylideneimine (Hpsal)] were characterized by physicochemical measurements and the molecular structure of the compound [$TcCl(psal)_2(PMe_2Ph)$] is reported.

Experimental

Materials.—Solutions of TcO_4^- in 0.1 mol dm^{-3} NH_4OH were purchased from the Radiochemical Centre, Amersham. The compounds [$AsPh_4$][$TcOCl_4$] and [$TcCl_4(PPh_3)_2$] were prepared following literature methods.[1,8] The Schiff bases, *N*-methylsalicylideneimine (Hmsal) and *N*-phenylsalicylideneimine (Hpsal), were prepared by mixing stoicheiometric quantities of salicylaldehyde and NH_2Me or NH_2Ph, respectively, in EtOH. The compound [$TcO(Cl)(psal)_2$] was obtained following methods described elsewhere.[1] Other materials used were commercially available reagent-grade chemicals.

Apparatus.—Elemental analyses for C, H, N, Tc, P, and Cl were performed as reported elsewhere.[9] I.r. spectra of samples in Nujol mulls, between CsI discs or in KBr pellets, were recorded on a Perkin-Elmer 580B spectrophotometer. Proton n.m.r. spectra in $CDCl_3$ solution were recorded on a 80-MHz Bruker spectrometer, while magnetic susceptibilities, of CH_2Cl_2 and CD_2Cl_2 solutions, were determined on the same spectrometer by Evans' method and corrected for ligand diamagnetism.

Syntheses.—*Chlorobis*(N-*methylsalicylideneiminato*)*oxotechnetium*(V). The compound [$AsPh_4$][$TcOCl_4$] (0.1 g) was dissolved in EtOH or MeOH (30 cm^3) and an excess of Hmsal (0.085 g) was then added. The reaction proceeded rapidly at room temperature and the colour changed suddenly from bright green to deep red. After 0.5 h the reaction solution was slowly evaporated in air and a red oil was obtained which was then dissolved in CH_2Cl_2. By evaporation of the resulting solution in air, deep red crystals of the final compound were formed and collected, washed with EtOH and Et_2O, and dried in air. Yield 90% (0.06 g). The product is soluble in CH_2Cl_2, $CHCl_3$, acetone and tetrahydrofuran (thf), and insoluble in EtOH, Et_2O, benzene, CCl_4, and pentane.

[$TcCl_4(Hmsal)_2$] *and* [$TcCl_4(Hpsal)_2$]. The compound [$TcCl_4(PPh_3)_2$] (0.1 g) was refluxed in toluene (40 cm^3) with an excess of ligand (0.07 g for Hmsal and 0.10 g for Hpsal) for 2 h. A precipitate was formed which, after cooling the reaction mixture, was filtered off, washed with hot toluene, CH_2Cl_2, thf, EtOH, and Et_2O, and dried in air. A red-violet microcrystalline solid was obtained, which was slightly soluble in acetone, but nearly insoluble in all the other common solvents. Yield 60% (0.04 g for the Hmsal complex, 0.05 g for the Hpsal complex).

[$TcCl_3(msal)(PPh_3)$] *and* [$TcCl_3(psal)(PPh_3)$]. The compound [$TcCl_4(PPh_3)_2$] (0.1 g) was dissolved in boiling toluene (40 cm^3) and to the resulting solution a stoicheiometric amount

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic positional parameters for [TcCl(psal)$_2$(PMe$_2$Ph)] with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Tc	0.210 8(1)	0.260 0(1)	0.634 1(0)	C(15)	0.071 0(15)	0.336 7(13)	0.715 0(4)
Cl	0.287 5(5)	0.472 2(3)	0.618 4(1)	C(16)	−0.006 7(15)	0.247 8(16)	0.735 2(4)
P	0.387 5(4)	0.185 2(4)	0.589 4(1)	C(17)	0.025 6(18)	0.235 0(18)	0.782 9(5)
O(1)	0.356 5(9)	0.253 4(10)	0.684 8(3)	C(18)	0.125 4(20)	0.311 9(19)	0.803 1(6)
O(2)	0.075 9(9)	0.271 6(8)	0.581 6(3)	C(19)	0.199 6(21)	0.397 8(19)	0.783 7(6)
N(1)	0.145 1(11)	0.077 0(9)	0.651 9(3)	C(20)	0.171 6(19)	0.415 1(17)	0.736 6(6)
N(2)	0.049 7(11)	0.342 4(10)	0.668 3(3)	C(21)	0.052 1(14)	0.001 8(12)	0.623 0(4)
C(1)	0.188 5(13)	0.022 0(12)	0.688 7(4)	C(22)	0.096 7(15)	−0.119 1(14)	0.611 9(5)
C(2)	0.290 4(13)	0.066 1(12)	0.721 6(4)	C(23)	0.001 4(17)	−0.194 5(15)	0.585 2(5)
C(3)	0.315 8(15)	−0.011 3(13)	0.759 0(5)	C(24)	−0.131 5(18)	−0.150 7(16)	0.571 7(5)
C(4)	0.424 4(17)	0.015 8(15)	0.790 7(5)	C(25)	−0.173 4(17)	−0.027 2(15)	0.581 7(5)
C(5)	0.511 0(17)	0.120 4(16)	0.786 6(5)	C(26)	−0.079 8(16)	0.050 7(14)	0.608 0(5)
C(6)	0.484 9(16)	0.200 7(13)	0.750 7(5)	C(27)	0.349 3(19)	0.244 2(21)	0.533 3(6)
C(7)	0.375 6(14)	0.174 1(13)	0.718 0(4)	C(28)	0.565 5(18)	0.245 2(19)	0.608 4(6)
C(8)	−0.028 9(14)	0.350 9(12)	0.572 6(4)	C(29)	0.413 2(18)	0.016 4(19)	0.584 3(6)
C(9)	−0.081 2(16)	0.365 4(14)	0.528 5(5)	C(30)	0.361 8(18)	−0.045 2(17)	0.546 8(6)
C(10)	−0.192 6(16)	0.448 4(15)	0.517 2(5)	C(31)	0.379 1(17)	−0.181 0(18)	0.545 7(7)
C(11)	−0.259 0(17)	0.514 9(15)	0.549 3(5)	C(32)	0.444 0(19)	−0.244 4(19)	0.581 2(5)
C(12)	−0.214 1(16)	0.498 1(14)	0.592 7(5)	C(33)	0.495 9(19)	−0.178 2(18)	0.618 4(6)
C(13)	−0.097 7(15)	0.418 2(13)	0.605 1(5)	C(34)	0.480 5(18)	−0.048 9(19)	0.619 4(5)
C(14)	−0.059 1(14)	0.404 1(13)	0.651 0(4)				

Table 2. Bond lengths (Å) and angles (°) in the 'inner core' of [TcCl(psal)$_2$(PMe$_2$Ph)]

Tc–Cl	2.427(4)	O(1)–C(7)	1.33(2)
Tc–O(1)	1.992(9)	C(7)–C(2)	1.41(2)
Tc–O(2)	1.975(9)	C(2)–C(1)	1.41(1)
Tc–N(1)	2.126(9)	N(1)–C(1)	1.31(1)
Tc–N(2)	2.132(10)	N(1)–C(21)	1.44(1)
Tc–P	2.412(4)	O(2)–C(8)	1.31(1)
P–C(27)	1.85(2)	C(8)–C(13)	1.44(2)
P–C(28)	1.85(2)	C(13)–C(14)	1.44(2)
P–C(29)	1.81(2)	N(2)–C(14)	1.29(2)
		N(2)–C(15)	1.44(1)
Cl–Tc–O(1)	89.5(3)	Tc–N(1)–C(1)	123.8(8)
Cl–Tc–N(1)	176.5(3)	N(1)–C(1)–C(2)	128.0(1.2)
Cl–Tc–O(2)	87.7(3)	C(1)–C(2)–C(7)	124.6(1.1)
Cl–Tc–N(2)	88.0(3)	C(2)–C(7)–O(1)	122.5(1.1)
Cl–Tc–P	87.1(1)	C(7)–O(1)–Tc	131.8(8)
P–Tc–O(2)	88.8(3)	Tc–N(1)–C(21)	121.5(7)
P–Tc–O(1)	88.4(3)	C(1)–N(1)–C(21)	114.7(1.0)
P–Tc–N(1)	95.0(3)	Tc–N(2)–C(14)	125.7(8)
P–Tc–N(2)	173.6(3)	N(2)–C(14)–C(13)	125.2(1.2)
O(1)–Tc–N(1)	87.8(4)	C(14)–C(13)–C(8)	123.3(1.2)
O(1)–Tc–O(2)	176.2(4)	C(13)–C(8)–O(2)	123.7(1.2)
O(1)–Tc–N(2)	95.7(4)	C(8)–O(2)–Tc	129.3(8)
O(2)–Tc–N(1)	95.0(4)	Tc–N(2)–C(15)	116.4(8)
O(2)–Tc–N(2)	86.8(4)	C(14)–N(2)–C(15)	117.7(1.1)
N(1)–Tc–N(2)	90.1(4)		

Table 3. Torsion angles and least-squares planes for [TcCl(psal)$_2$(PMe$_2$Ph)]

(*a*) Principal torsion angles (°)

Tc–N(1)–C(1)–C(2)	−4.5	Tc–N(2)–C(14)–C(13)	6.0
N(1)–C(1)–C(2)–C(7)	−7.2	N(2)–C(14)–C(13)–C(8)	8.3
C(1)–C(2)–C(7)–O(1)	7.9	C(14)–C(13)–C(8)–O(2)	−0.7
C(2)–C(7)–O(1)–Tc	4.0	C(13)–C(8)–O(2)–Tc	−22.7

(*b*) Equations of least-squares planes in the form $M_1X + M_2Y + M_3Z = D$; displacements (Å) of relevant atoms are in square brackets

Plane		M_1	M_2	M_3	D
1	Cl, O(1), N(1), O(2)	0.733	−0.381	−0.563	−12.010
	[Cl −0.01, O(1) 0.05, N(1) −0.06, O(2) 0.04, Tc 0.00, C(1) −0.26, C(2) −0.37, C(7) −0.14]				
2	N(1), C(1), C(2), C(7), O(1)	0.735	−0.514	−0.441	−9.729
	[N(1) 0.00, C(1) 0.02, C(2) −0.03, C(7) 0.03, O(1) −0.01, Tc −0.26, C(21) 0.21]				
3	O(2), C(8), C(13), C(14), N(2)	0.640	0.765	−0.076	0.180
	[O(2) −0.01, C(8) 0.03, C(13) 0.02, C(14) −0.06, N(2) 0.03, Tc 0.48, C(15) −0.09]				
4	C(2)—C(7)	0.681	−0.550	−0.484	−10.777
5	C(8)—C(13)	0.646	0.761	−0.064	0.402
6	C(15)—C(20)	0.718	−0.683	−0.136	−6.505
7	C(21)—C(26)	0.449	0.364	−0.816	−16.284
8	C(29)—C(34)	0.922	0.113	−0.370	−4.646

(*c*) Dihedral angles (°) between planes

1–2	10.4	1–7	49.5	2–4	4.4	3–5	0.8
1–3	77.2	1–8	32.7	2–7	59.8	3–6	93.0
1–6	30.4	2–3	83.6	2–8	38.4	3–8	45.2

(*d*) Interatomic contact distances (Å) in the octahedral environment

Cl···O(1)	3.13	P···O(1)	3.08	O(1)···N(2)	3.06
Cl···O(2)	3.07	P···N(1)	3.35	O(2)···N(1)	3.03
Cl···N(2)	3.17	P···O(2)	3.08	O(2)···N(2)	2.82
Cl···P	3.34	O(1)···N(1)	2.86	N(1)···N(2)	3.01

of the ligand (0.018 g for Hmsal and 0.026 g for Hpsal) was added. After refluxing for 2 h the reaction solution was cooled and a red-violet solid, corresponding to the disubstituted technetium(IV) complex described above, was filtered off. The filtrate was slowly evaporated in air, producing a brown oil, which was dissolved in acetone–ethanol. Evaporation of the resulting solution in air gave brown crystals of the final compound, which were washed with EtOH and Et$_2$O and dried in air. Yield 40% (0.032 g for the msal complex, 0.035 g for the psal complex). The compounds are soluble in CH$_2$Cl$_2$, CHCl$_3$, acetone, and thf, and insoluble in EtOH, Et$_2$O, CCl$_4$, and pentane.

[TcCl(msal)$_2$(PMe$_2$Ph)] *and* [TcCl(psal)$_2$(PMe$_2$Ph)]. The compounds [TcO(Cl)(msal)$_2$] or [TcO(Cl)(psal)$_2$] were dissolved in boiling benzene (30 cm^3) under a nitrogen stream. To this solution was added an excess (0.15 g) of PMe$_2$Ph and after refluxing for 2 h the solution was filtered off and evaporated in air. A red oil was produced and then dissolved in CH$_2$Cl$_2$–EtOH. The resulting solution, slowly evaporated in air, gave red crystals of the final compound, which were washed with EtOH

Table 4. General properties and elemental analyses for the complexes

		Analysis[a]/%				
Complex	Colour	C	H	N	Cl	Tc
$[TcO(Cl)(msal)_2]$	Red	46.15	4.10	6.40	9.20	25.0
		(45.9)	(3.85)	(6.70)	(8.45)	(23.65)
$[TcCl_3(msal)(PPh_3)]$[b]	Brown	52.1	4.00	2.30	18.05	15.5
		(52.9)	(3.85)	(2.35)	(17.65)	(16.45)
$[TcCl_3(psal)(PPh_3)]$[c]	Brown	55.95	3.5	2.00	16.85	13.9
		(56.1)	(3.80)	(2.10)	(16.0)	(14.9)
$[TcCl_4(Hmsal)_2]$	Red-violet	38.0	3.85	5.90	28.45	20.5
		(37.6)	(3.55)	(5.50)	(27.75)	(19.35)
$[TcCl_4(Hpsal)_2]$	Red-violet	50.05	4.00	4.00	22.85	17.0
		(49.15)	(3.50)	(4.40)	(22.3)	(15.6)
$[TcCl(msal)_2(PMe_2Ph)]$	Red	53.35	5.75	5.25	6.20	19.95
		(53.3)	(5.05)	(5.20)	(6.55)	(18.3)
$[TcCl(psal)_2(PMe_2Ph)]$	Red	64.3	4.65	4.15	5.80	16.9
		(64.4)	(4.95)	(4.40)	(5.60)	(15.6)

[a] Calculated values in parentheses. [b] P 5.85 (5.15)%. [c] 5.10 (4.65)%.

Table 5. Some important i.r. bands and proton chemical shifts (with respect to $SiMe_4$) for the complexes

	I.r. (cm^{-1})					^1H n.m.r. (p.p.m.)		
Complex	Tc=O	C=N	C–O	Tc–P	Tc–Cl	$P-CH_3$	$P-CH_3$	$\mu_{eff.}$
$[TcO(Cl)(msal)_2]$	940vs	1 610vs	1 290vs		300m			Diamagnetic
$[TcCl_3(msal)(PPh_3)]$		1 600vs	1 280s	1 090m	340s			3.7
$[TcCl_3(psal)(PPh_3)]$		1 595vs	1 300s	1 090m	345s			3.7
$[TcCl_4(Hmsal)_2]$		1 650vs	1 275s		320s			3.7
$[TcCl_4(Hpsal)_2]$		1 630vs	1 270s		330vs			3.7
$[TcCl(msal)_2(PMe_2Ph)]$		1 588vs	1 290s		280w	−15.00	−24.40	2.5
$[TcCl(psal)_2(PMe_2Ph)]$		1 580vs	1 290s		295w	−16.25	−25.60	2.5

(10 cm^3) and pentane, and dried in air. Yield 90% (0.12 g for msal complex, 0.14 g for psal complex). The compounds are soluble in CH_2Cl_2, $CHCl_3$, acetone, thf, and CH_3CN, slightly soluble in EtOH, MeOH, and Et_2O, and insoluble in CCl_4 and pentane.

X-Ray Crystallography.—The compound $[TcCl(psal)_2(PMe_2Ph)]$ crystallizes as deep red parallelepipeds from CH_2Cl_2. A large needle specimen of approximate dimensions 0.20 × 0.10 × 0.25 mm was selected for data collection on a Philips PW 1 100 automated diffractometer using Mo-K_α radiation (λ = 0.710 7 Å). 5 716 Reflections were collected (scan mode, θ—2θ; scan width, 1.1°; scan rate, 0.03° s^{-1}; background time, 16 s) at room temperature up to $2\theta = 50°$ and averaged 4 734 independent reflections.

Crystal data. $C_{34}H_{31}ClN_2O_2PTc$, $M = 664.7$, monoclinic, space group $P2_1/c$, $a = 9.500(4)$, $b = 10.596(4)$, $c = 31.000(9)$ Å, $\beta = 95.59(5)°$, $U = 3\ 105.7(2.0)$ Å^3, $Z = 4$, $D_c = 1.422$ g cm^{-3}, $F(000) = 1\ 360$. Three intense reflections near $\chi = 90°$ were examined at 10° intervals over the range $0 < \psi < 360°$. A plot of observed intensities about these three diffraction vectors showed only random counting deviations and the absorption corrections ($\mu = 6.2\ cm^{-1}$) were therefore omitted.

The structure was solved by repeated Patterson and Fourier syntheses and refined by least-squares methods.[10] Only the three heavy atoms were refined anisotropically, with unit weights, assigned to the 2 500 observed reflections with $I > 3\sigma(I)$, and refinement yielded $R = 0.071$, with a maximum shift in the last cycle of 0.06σ. In the final difference map the largest peak (0.8 e Å^{-3}) was at the middle of the C(31)–C(32) bond in the phenyl group of PMe_2Ph, which shows the highest thermal motion, and so was not particularly significant. Final positional parameters are listed in Table 1, selected bond lengths and angles in Table 2, and some torsion angles and relevant least-squares planes in Table 3.

Results and Discussion

Elemental analyses for the complexes are given in Table 4, while i.r., ^1H n.m.r., and magnetic susceptibility data are reported in Table 5.

Technetium(IV).—The synthesis of complexes with bidentate Schiff-base ligands, by substitution reactions of the well characterized $[Tc^{IV}Cl_4(PPh_3)_2]$ and $[Tc^{IV}Cl_6]^{2-}$ complexes, gave rise to new products from the former complex, and the known salicylaldehyde (Hsal) complex $[TcCl_4(sal)]^-$ [11] from the latter. The Hsal molecule arises from the hydrolysis of the bidentate Schiff-base ligand. The complexes isolated have the general formulae $[TcCl_4(HL)_2]$ and $[TcCl_3L(PPh_3)]$ (HL = Hmsal or Hpsal).

The complexes $[TcCl_4(HL)_2]$ were produced by treating $[TcCl_4(PPh_3)_2]$ with an excess of ligand. This resulted in the formation of disubstituted complexes containing two unidentate Schiff bases, co-ordinated to the Tc^{4+} centre through the aldimine nitrogen. These compounds are particularly inert and they do not transform to the corresponding disubstituted chelate complexes through attack by the phenolic oxygen of the ligand, in boiling toluene. This may be partly due to the low solubility and the ease of isolation of the complexes $[TcCl_4(HL)_2]$ under the conditions reported here. Analogous behaviour was observed for the rhenium(IV) complexes $[ReCl_4(HL)_2]$.[12] When the $[TcCl_4(PPh_3)_2]$: ligand ratio was set equal to unity, the monosubstituted chelate complexes $[TcCl_3L(PPh_3)]$ were obtained, resulting from the substitution of a chloride and PPh_3 group of the starting compound by the bidentate Schiff base. The same complexes were observed for rhenium(IV), but in this case the intermediate monosubstituted complexes $[ReCl_4(HL)(PPh_3)]$ were also isolated, in which the Schiff base is co-ordinated to the metal only through the neutral aldimine nitrogen.[12] Intermediate monosubstituted complexes were not observed for Tc^{IV} under the same conditions.

I.r. spectra of the complexes $[TcCl_4(HL)_2]$ show the ν(C=N) stretching frequency in the range 1 630—1 650 cm^{-1}, characteristic of a unidentate Schiff base co-ordinated only through the aldimine nitrogen,[12–14] while ν(O–H) is found in the range 3 000—3 100 cm^{-1}. The ν(Tc–Cl) vibration falls in the range 320—330 cm^{-1}, and has the form of a very intense, broad band in which the eventual fine structure is collapsed, preventing any determination of the number of metal–halogen stretching frequencies and, therefore, structural assignments. Magnetic susceptibility measurements in solution gave a value of $\mu_{eff.}$ = 3.7 as expected for a d^3 system in an octahedral environment. The resulting paramagnetism of these technetium(IV) complexes strongly affects the ^1H n.m.r. spectrum, shifting the signals up- and down-field with respect to the $SiMe_4$ reference peak and broadening the linewidth, so that no certain proton assignments can be made. The linewidth for complexes $[TcCl_4(HL)_2]$ (30 Hz) is greater than that found for the analogous rhenium(IV) complexes (20 Hz), in agreement with theoretical predictions.[15] On the basis of the spectral findings, precise configurations cannot be attributed to the complexes $[TcCl_4(HL)_2]$. The two possible structures are: (*a*) the two Schiff-base ligands in *trans* positions and the four halogens in the same plane, or (*b*) the two Schiff-base ligands in *cis* positions and the four halogens occupying the vertices of two adjacent faces of the octahedron.

I.r. spectra of the complexes $[TcCl_3L(PPh_3)]$ show ν(C=N) vibrations in the region 1 595—1 600 cm^{-1}, characteristic of a chelate Schiff base,[12–14] while ν(Tc–P) is at 1 090 cm^{-1}. A strong, broad band is observed in the range 340—345 cm^{-1} and is attributed to the ν(Tc–Cl) vibration. Owing to the broadness of this band, it was difficult to evaluate the precise number of stretching frequencies for the Tc–Cl bond. Thus, no choice could be made between the two possible halogen *mer* or *fac* configurations of the complexes $[TcCl_3L(PPh_3)]$. This situation contrasts with that found for the analogous rhenium(IV) complexes $[ReCl_3L(PPh_3)]$, for which the presence of three bands in the metal–halogen stretching region led to the assignment of a *mer* configuration to the halogens.[12] The same value of $\mu_{eff.}$ = 3.7 was measured in solution for complexes $[TcCl_3L(PPh_3)]$ as well as $[TcCl_4(HL)_2]$ and thus analogous considerations apply to the discussion of their ^1H n.m.r. spectra. These results again prevent the assignment of a precise configuration to this class of compounds.

Technetium(III).—While the rhenium(V) compounds $[ReO(Cl)L_2]$ (L = msal or psal)[16] do not react with PMe_2Ph,[17] the corresponding oxotechnetium(V) complexes $[TcO(Cl)L_2]$ are reduced by the same phosphine group to give technetium(III) complexes of the type $[TcClL_2(PMe_2Ph)]$ in which a PMe_2Ph group has replaced the oxygen atom of the Tc≡O triple bond. The probable equation for the reaction is (1). The reaction may

$$[TcO(Cl)L_2] + 2\ PMe_2Ph \longrightarrow [TcClL_2(PMe_2Ph)] + OPMe_2Ph \quad (1)$$

be regarded as proceeding *via* initial removal of the oxo-oxygen group by a PMe_2Ph molecule, to form $OPMe_2Ph$, and subsequent addition of a second phosphine group in the vacant position. However, the details of the structure of the complex $[TcCl(psal)_2(PMe_2Ph)]$ (see below) reveal that the positions of the two Schiff-base ligands in the final reduced complex are changed with respect to the starting compound, indicating the occurrence of a rearrangement of the co-ordinated ligands during the reduction reaction. In particular, the phenolic oxygens of the two Schiff bases are found in *trans* positions in the reduced complex, while in $[TcO(Cl)(psal)_2]$ they were found in *cis* positions.[1]

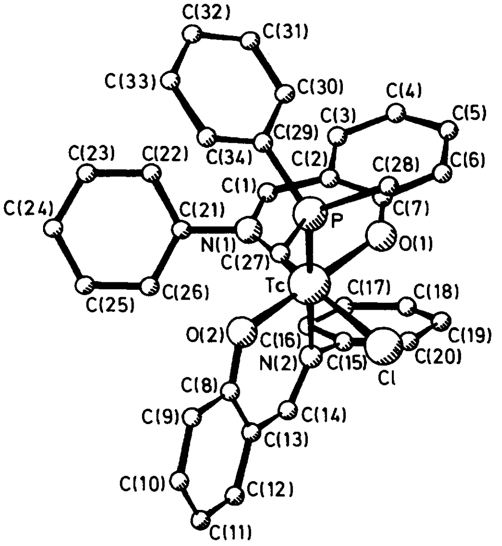

Figure. PLUTO drawing of $[TcCl(psal)_2(PMe_2Ph)]$ viewed along the bisector of the P–Tc–N(2) angle

The value of $\mu_{eff.}$ = 2.5 measured in solution, is in agreement with a d^4 octahedral system with two unpaired electrons.[17] The resulting paramagnetism, as in the case of technetium(IV) complexes, shifts the ^1H n.m.r. proton signals up- and down-field relative to the $SiMe_4$ reference peak and broadens the linewidths, but here some assignments can be made (Table 5). The linewidths are sharper (20 Hz) than for Tc^{IV}–L compounds, but broader than those for rhenium(III) complexes with the same ligands (7 Hz).[17] The resonances at $\delta = -15.00$ and -24.40 p.p.m. for the complex $[TcCl(msal)_2(PMe_2Ph)]$ and at $\delta = -16.25$ and -25.60 p.p.m. for the complex $[TcCl(psal)_2(PMe_2Ph)]$ were attributed to the two methyl groups on the phosphine ligand. These signals arise when the complex does not possess a symmetry plane passing through the Tc–P atoms, so that the shielding experienced by the two methyl groups on the same phosphine differs significantly, even admitting free rotation around the Tc–P bond.[18] The absence of this symmetry element leads to the conclusion that, in $[TcClL_2(PMe_2Ph)]$ complexes, the two Schiff bases are not in the same plane of the octahedron, a fact confirmed by crystallographic data.

X-*Ray Structure of Chloro*(*dimethylphenylphosphine*)*bis*(N-*phenylsalicylideneiminato*)*technetium*(III).—The structure of $[Tc^{III}Cl(psal)_2(PMe_2Ph)]$ consists of well separated molecules with no significant intermolecular interactions. The two *N*-phenylsalicylideneiminato moieties each act as bidentate O- and N-donor ligands to the Tc atom, which is in a distorted octahedral co-ordination environment. The chelate ligands are almost mutually orthogonal (83.6°), one ligand bridging two contiguous positions in the plane normal to the Tc–Cl bond, the other in the plane normal to the Tc–P bond, as depicted in the Figure. The nitrogen atom of one ligand is located in a position *trans* to the phosphine group, while the O(1), N(1), O(2), and Cl atoms define a plane containing the Tc atom. The structural parameters listed in Table 2 are quite normal[1,2,4,11,19,20] and they do not merit any comment. The distortion of the 'inner core' from an ideal Tc-centred octahedron is mainly evidenced by the P–Tc–N(2) angle [173.6(3)°]; the stereochemistry is not as dramatically distorted as in the parent complex $[Tc^VO(Cl)(p\text{-}sal)_2]$[1] and the 'bite' angles of the bidentate ligands, O(1)–Tc–N(1) and O(2)–Tc–N(2), approach 90° (87.8 and 86.8° respectively).

Conclusions

As reported here, the disubstituted Schiff-base–oxo complexes $[TcO(Cl)L_2]$ are reduced by PMe_2Ph to give the corresponding technetium(III) disubstituted complexes $[TcClL_2(PMe_2Ph)]$. The analogous rhenium(V) oxo-complexes $[ReO(Cl)L_2]$ are completely inert to such a reduction reaction under the same conditions.[17] Moreover, the monosubstituted $[TcOCl_3L]^-$ complexes are strongly affected by the reducing power of PMe_2Ph and are easily converted into $[TcCl_3(PMe_2Ph)_3]$, with loss of the co-ordinated base. The analogous $[ReOCl_3L]^-$ complexes, instead, give rise to the products $[Re^VOCl_2L(PMe_2Ph)]$, $[Re^{III}Cl_2L(PMe_2Ph)_2]$, and $[Re^{III}Cl_3(PMe_2Ph)_3]$, by simply increasing the phosphine:metal stoicheiometric ratio.[14]

These findings are in agreement with the observed behaviour of technetium and rhenium with respect to their reactions with phosphines. It was found[8] that the reactions of pertechnetate with dialkylphenylphosphines PR_2Ph (R = Me or Et) yielded two types of compounds $[TcX_4(PR_2Ph)_2]$ and $[TcX_3(PR_2Ph)_3]$ (X = Cl or Br) depending on the Tc:PR_2Ph ratio. With triphenylphosphine (PPh_3) only the complex $[TcCl_4(PPh_3)_2]$ was obtained even at very low Tc:PPh_3 ratios. The behaviour of rhenium in these reactions is unlike that of technetium. In fact, with PR_2Ph, after a prolonged reaction time, the complexes $[ReX_3(PR_2Ph)_3]$ can be obtained,[21] while with PPh_3 only $[ReOX_3(PPh_3)_2]$ was observed.[22] These results can be attributed to the easier reduction of technetium to the +4 and +3 oxidation states than of rhenium.

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