Synthesis and Characterization of Neutral Technetium(III) Complexes with Mixed S,P-Bidentate Phosphine–Thiolate Ligands. Crystal Structure of [Tc(SCH$_2$CH$_2$PPh$_2$)$_2$-(SCH$_2$CH$_2$PPh$_2$O)]†

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Reduction–substitution reactions of [TcO$_4$]$^-$ with an excess of the mixed bidentate thiol–phosphine ligands HL^n [L^1 = 2-(diphenylphosphino)ethanethiolate; L^2 = 2-(diphenylphosphino)propanethiolate and L^3 = 2-(diphenylphosphino)thiophenolate] gave neutral five-co-ordinate technetium(III) complexes of the type [TcL$^n{}_2$(O=L^n)] (n = 1 **1** or 2 **2**). However, the aromatic phosphine–thiol ligand (n = 3) gave six-co-ordinated [TcL$^3{}_3$] **3**. The five-co-ordinated complexes are diamagnetic and exhibit a trigonal-bipyramidal geometry in which two π-acid phosphorus donors of two chelates are co-ordinated mutually *trans* in the axial positions, with the corresponding thiolate sulfur atoms on the equatorial plane. A further thiolate group completes the basal-plane co-ordination leaving a pendant phosphorus donor outside the co-ordination sphere. This is oxidized to phosphine oxide, which was revealed by a crystal structure determination of **1**: triclinic, space group $P\bar{1}$, with Z = 2, a = 9.991(4), b = 12.417(4), c = 18.687(8) Å, α = 73.37(3), β = 76.88(3) and γ = 73.68(3)°; R converged to 0.0703 using 2765 observed reflections. In addition, the compounds were characterized by elemental analysis, IR, ^{1}H and ^{31}P NMR, UV/VIS and FAB spectroscopies and cyclic voltammetric measurements. The occurrence of trigonal-bipyramidal *vs.* octahedral geometry is discussed in terms of ligand steric requirements and electronic factors governing the metal–donor interactions.

Sulfur and phosphorus are ideal donor atoms for technetium, as demonstrated by the extensive co-ordination chemistry exhibited by this Group VII metal with thiols and tertiary phosphines.[1] Usually, mono- and bi-dentate thiolate ligands stabilize technetium in oxidation states ranging from V to III. The complexes consistently adopt a square-pyramidal geometry[2] for d^2 configurations and octahedral, trigonal-prismatic[3] or trigonal-bipyramidal arrangements[4,5] for d^4 species. On the other hand, mono- and bi-dentate tertiary phosphines co-ordinate preferentially to a technetium(III) ion in a more or less distorted octahedral environment.[1] The combination of thiol and diphosphine ligands has also produced a variety of mixed thiolatophosphinetechnetium(III) complexes, which usually show a *trans*-[Tc(L–L)$_2$X$_2$]$^+$ array[6,7] (L–L = diphosphine, X = $^-$SR), however Tc$^{\text{II}}$ and/or *cis* geometries are accessible depending upon the substituents on the phosphorus and sulfur donors.[7,8]

Despite the well developed thiolate and phosphine technetium chemistry, studies on the reactivity of mixed polydentate phosphine–thiol ligands towards technetium[9–11] (and moreover toward transition metals[12,13]) have appeared in the literature only recently. The paucity of investigations in this area probably reflects the lack of commercially available functionalized phosphines, the synthesis of which requires a multistep approach and/or tedious procedures.[14] Nevertheless, this class of heterodonor ligands possesses enhanced co-ordination ability by virtue of the chelate effect and retains the reductive ability typical of P$^{\text{III}}$.[15] For example, the mixed phosphine–thiol aromatic ligand P(C$_6$H$_4$SH-*o*)$_3$, a potentially tetradentate 'umbrella type' chelate, reacts with [TcO$_4$]$^-$ or [TcOCl$_4$]$^-$ in the presence of Pr^{i}NC to give a five-co-ordinate trigonal-bipyramidal, as well as six-co-ordinate octahedral, technetium(III) species of the type [Tc{P(C$_6$H$_4$S-*o*)$_3$}(CNPr^i)$_n$] (n = 1 or 2).[9] Moreover, the potentially bidentate ligand PPh$_2$(C$_6$H$_4$SH-*o*) (HL^3), utilizing a similar reduction–substitution reaction with [TcO$_4$]$^-$ or [TcCl$_4$(PPh$_3$)$_2$], yields the trisubstituted octahedral *mer*-[TcL$^3{}_3$] complex.[10,11]

In this paper we report on the reactivity of the mixed bidentate phosphine–thiols Ph$_2$PCH$_2$CH$_2$SH (HL^1) and Ph$_2$PCH$_2$CH$_2$CH$_2$SH (HL^2) towards pertechnetate. The resulting five-co-ordinate, diamagnetic technetium(III) complexes [TcL$^n{}_2$(O=L^n)] (n = 1 **1** or 2 **2**) exhibit a trigonal-bipyramidal configuration with two ligands co-ordinated through both P and S donors and the remaining one *via* the thiolate sulfur only, as evidenced by a crystal structure determination of [TcL$^1{}_2$(O=L^1)] **1**. The formation of trigonal-bipyramidal as opposed to octahedral geometry is qualitatively discussed in terms of ligand steric constraints and electronic factors which govern the metal–ligand interaction. This behaviour is compared with other mixed phosphine–thiolate and polydentate phosphine–thiolate technetium complexes previously reported.

This work is part of an extensive study we have been pursuing with functionalized phosphines.[10,16–19] Previous investigations have demonstrated that compounds of the general formula

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: Ci = 3.7 × 10^{10} Bq.

Ph_2PRCO_2H (R = CH_2, C_2H_4 or *o*-C_6H_4) or $PPh_2(C_6H_4OH$-*o*) incorporating a soft phosphorus(III) donor and a hard carboxylic or hydroxyl group always leads to homoleptic octahedral *mer*-$[Tc^{III}(P–O)_3]$ complexes.[10,19] Conversely, the design of totally soft–soft PS-functionalized phosphines allows the synthesis of technetium(III) species of different geometries by varying the nature of the carbon chain interposed between the phosphorus and sulfur donors.

Results and Discussion

Synthesis.—The bidentate phosphine–thiols HL^n (n = 1–3) readily react with $[NH_4][TcO_4]$ or $[TcOCl_4]^-$ in EtOH to give neutral technetium(III) complexes of various geometries depending on the nature of the carbon chain joining the S and P donor atoms. In particular, the mixed PS-aliphatic ligands (HL^1 and HL^2) stabilize five-co-ordinate species which adopt a trigonal-bipyramidal configuration, whereas the mixed PS-fully aromatic ligand HL^3 affords a six-co-ordinate complex which exhibits a distorted-octahedral geometry. All the reactions are conducted using an excess of ligand; reducing the ligand : metal ratio below 4 : 1 causes a drastic reduction in yields. Equations (1) and (2) illustrate probable stoichiometries for the reduction–substitution reactions of the PS-aliphatic ligands.

$$[NH_4][TcO_4] + 4HL^n \longrightarrow [TcL^n_2(O{=}L^n)] + HL^n{=}O + NH_4OH + H_2O \quad (1)$$

$$[NBu^n_4][TcOCl_4] + 3HL^n \longrightarrow [TcL^n_2(O{=}L^n)] + 3HCl + [NBu^n_4]Cl \quad (2)$$

In these reactions the phosphine–thiol functions both as reductant and co-ordinating agent. In equation (1), 2 mol of ligand are consumed for the reduction of Tc^{VII} to Tc^{III} with the concomitant production of phosphine oxide. Complexes **1** and **2** can also be prepared by redox/substitution reactions starting from the pre-reduced precursor $[TcOCl_4]^-$. There is no evidence for the formation of technetium(V) complexes at room temperature as occurs with the third-row congener rhenium which gives $[ReOClL^2_2]$.[13] From equation (2) it appears that 1 mol of oxidized ligand is retained in the ligating sphere, through co-ordination of the thiolate function alone. The metal is saturated by two further phosphine–thiolate ligands which, on the contrary, act as bidentate chelates. The latter mechanism is confirmed by the high yields (> 95%) obtained when using the technetium(V) starting material in the stoichiometric ratio 1 : 3 (Tc : L^n) (n = 1 or 2).

It has to be noted that reduction–substitution reactions of both $[TcO_4]^-$ or $[TcOCl_4]^-$ always involve the extraction of one or more oxygen atoms by the phosphine reductant. The reaction mechanism with $[TcOCl_4]^-$ most likely involves the substitution of chlorides for thiolate groups[5,20] followed by reduction of the metal centre by the P^{III} of one chelate through oxygen extraction. The production of a phosphine oxide group may prevent further co-ordination of such a moiety to the metal, forcing the technetium ion to be five-co-ordinated. In addition, when the reaction conditions are not rigorously controlled, the phosphorus atom may, at least partially, oxidize in the reaction mixture (or the possible presence of a phosphine oxide species in the free ligand) and prevent the formation of a six-co-ordinate complex. In order to force the tris co-ordination of alkylphosphinethiolate chelates, ligand-exchange reactions starting from the labile technetium(III) precursor $[TcCl_3(MeCN)(PPh_3)_2]$ have been conducted in dry and degassed solvents (EtOH or MeCN) using an excess of pure (^{31}P NMR spectroscopy) HL^1 under strictly anaerobic conditions. The reactions gave a mixture of products one of which is identifiable as a five-co-ordinate complex analogous to **1**, and any attempt at purification by recrystallization of the mixture always leads to the formation of **1**. Therefore, the obtainment of a five-co-ordinate species appears to be a general feature when treating Tc with alkylphosphine–thiolate ligands, and the presence of a phosphine oxide pendant group seems to be irrelevant in determining the final co-ordination sphere. Such a behaviour is totally confirmed when the ligand-exchange reaction is conducted with the third-row rhenium complex $[ReCl_3(MeCN)(PPh_3)_2]$ and HL^1.[21] On the other hand, the availability of the pendant P or P=O groups and the ability of the thiolate sulfurs to act as bridging ligands raises the possibility that these complexes could be capable of binding additional metal ions,[22] but only monomeric species have been characterized whereas the presence of polymeric compounds was not clearly evidenced.

The ligand HL^3 reacts in a similar reduction–substitution pathway to equation (1) starting from pertechnetate and following the stoichiometry in equation (3).

$$[NH_4][TcO_4] + 5HL^3 \longrightarrow [TcL^3_3] + 2HL^3{=}O + NH_4OH + H_2O \quad (3)$$

Characterization.—The technetium(III) complexes prepared in this work have been characterized by (*i*) elemental analyses which are in agreement with the proposed formulations, (*ii*) conductivity measurements, which show values consistent with neutral complexes, (*iii*) spectroscopic measurements including IR, UV/VIS, NMR, positive-ion FAB mass and a crystal structure determination. The IR spectra of the five-co-ordinate complexes **1** and **2** show a very strong absorption around 1100 cm^{-1}, which is assigned to the ν(P=O) stretching vibration, and a number of absorptions characteristic of the phenylphosphine moieties. No bands assignable to ν(Tc=O) are observed in the range 1000–880 cm^{-1} confirming the absence of any oxotechnetium(V) species. The formulation of the compounds is further established by the positive-ion FAB^+ mass spectra which show ions at m/z = 851 for $[TcL^1_2(O{=}L^1)]$, at m/z = 893 for $[TcL^2_2(O{=}L^2)]$ and at m/z 980 for $[TcL^3_3]$. Several fragment ions corresponding to the loss/addition of oxygen and loss of L^n units are also observed, as detailed in Table 1. Both **1** and **2** exhibit similar and characteristic absorption bands in the electronic spectra while, as expected on the basis of the different co-ordination, the UV/VIS spectrum of $[TcL^3_3]$ shows a very different pattern dominated by an intense absorption in the visible region at 605 nm. The spectral data are summarized in Table 1 and the visible spectra of **1** and **3** are depicted in Fig. 1.

The NMR signals are strongly dependent on the magnetic properties of the complexes. Therefore, the paramagnetism of the d^4 ion in the octahedral high-spin $[TcL^3_3]$ complex, confirmed by susceptibility measurements which shows a value in agreement with a high-spin d^4 system, does not allow a ^{31}P signal to be recorded, whereas the ^1H NMR spectrum shows a multiplet in the aromatic region (δ 6.2–8.2) along with a broad resonance centred at δ 13.0. Conversely, according to their trigonal-bipyramidal configuration, **1** and **2** are diamagnetic species. The ^{31}P-{^1H} spectra show two distinct resonances, a sharp singlet and an unresolved multiplet, in accordance with the presence in the molecule of two inequivalent phosphorus environments. Usually, the resonance arising from the P^V of a phosphine oxide group of a tertiary phosphine is shifted downfield with respect to the corresponding P^{III} of the unoxidized phosphine.[23] However, in corresponding complexes, the attribution of the phosphorus signals is not straightforward. Nevertheless, the sharp singlet may be tentatively assigned to unco-ordinated phosphine oxide for the following reasons: (*i*) the pure singlet, apart from the proton coupling buried in the ^{31}P-{^1H} experiments, is indicative of no other heterocouplings; (*ii*) the chemical environment surrounding the pendant P=O group in the five-co-ordinate technetium species does not differ significantly from that in free phosphine oxide. Consequently, the related signals should fall in a relatively narrow range (the free oxidized ligands show the values δ 38.6 and 40.6 for HL^1

Table 1 The NMR,* UV/VIS (λ/nm, ε/dm^3 mol^{-1} cm^{-1}) and FAB$^+$ spectral data

	NMR (chloroform)						
	^{31}P		^{1}H			UV/VIS (dichloromethane), λ (ε)	FAB$^+$, *m*/*z* (relative intensity in %)
Compound	P^{III}	P^{V}	Aromatic	Aliphatic	SH		
HL^1	−20		7.30–7.50 (m)	2.62 (m), 2.39 (m)	1.67 (dt)		
HL^2	−19		7.30–7.50 (m)	2.63 (q), 2.16 (m), 1.76 (m)	1.34 (t)		
HL^3	−14.7		6.70–7.50 (m)	—	4.00 (s)		
1 [TcL$^1_2$(O=L^1)]	+69.9 (m)	+27.7 (s)	7.05–7.60 (m)	1.90–3.10 (various m)	—	540 (2400), 490 (2000), 365 (6100), 330 (5700), 295 (19 300)	851 (42, *M*$^+$), 835 (16, *M*$^+$ − O), 621 (100, *M*$^+$ + O − L), 605 (24, *M*$^+$ − L)
2 [TcL$^2_2$(O=L^2)]	+22.4 (m)	+31.4 (s)	7.20–7.90 (m)	1.50–3.10 (various m)	—	550 (1000), 490 (1200), 370 (4100), 295 (10 200)	893 (67, *M*$^+$), 649 (100, *M*$^+$ + O − L), 633 (78, *M*$^+$ − L)
3 [TcL$^3_3$]	n.d.	—	6.20–8.20 (m) 13.00 (br s)	—	—	605 (7000), 410 (3250), 290 (10 600)	980 (51, *M*$^+$), 687 (100, *M*$^+$ − L)

* Chemical shifts in ppm with multiplicities in parentheses. s = Singlet, t = triplet, dt = doublet of triplets, q = quartet, m = multiplet, br = broad, n.d. = not detectable.

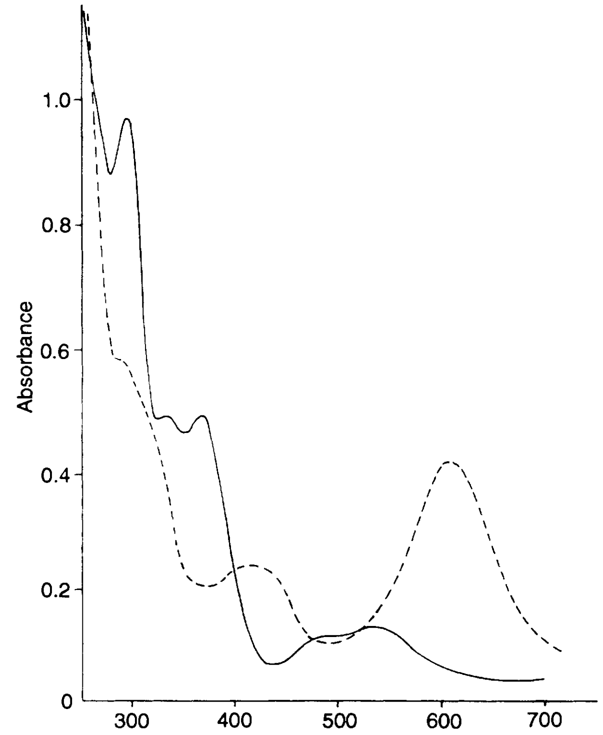

Fig. 1 The UV/VIS spectra (700–250 nm) of 10^{-5} mol dm^{-3} solutions of complexes **1** (——) and **3** (– – –) in CH$_2$Cl$_2$

and HL^2, respectively). Therefore, the unresolved multiplet must arise from the co-ordinated P^{III} atoms. Steric factors imposed by the geometry of the aliphatic PS-ligands (*i.e.* five- or six-membered chelate ring) induce a different overlap of the pertinent orbitals of P and Tc which in turn causes the associated ^{31}P signal to move from δ 69.9 for **1** to 22.4 for **2**. The ^{1}H NMR spectra of **1** and **2** exhibit signals due to the arylphosphine and the methylene protons of the aliphatic chain in the appropriate regions and in the correct integration ratio.

Positive-ion FAB$^+$ mass spectra of the mixture obtained upon reaction of [TcCl$_3$(MeCN)(PPh$_3$)$_2$] with an excess of HL^1 under anaerobic conditions show no mass ions higher than *m*/*z* 835, which corresponds to a complex containing three ligands. The ^{31}P-{^{1}H} NMR spectrum of the resulting mixture indicates the presence of one major diamagnetic species which gives two signals: a multiplet centred at δ 71.8 and a singlet at −5.9. The deshielded signal is in good agreement with the values exhibited by the co-ordinated phosphorus atoms in **1**, whereas the upfield signal is significantly shielded with respect to the values arising from the pendant phosphine oxide group. In addition, the upfield signal approaches values typical of P^{III} in unco-ordinated diarylmonoalkylphosphines. These data strongly support a co-ordination geometry for the raw complex similar to the trigonal-bipyramidal array exhibited by **1** and **2**, but with a pendant unoxidized phosphine group.

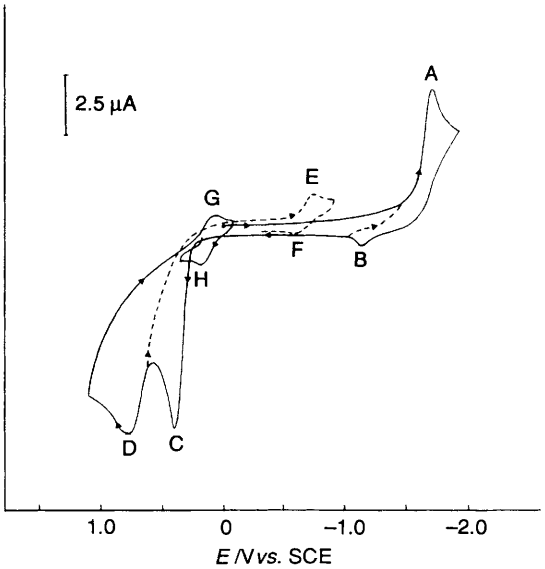

Fig. 2 Cyclic voltammetric scan of 10^{-3} mol dm^{-3} complex and 0.1 mol dm^{-3} [NEt$_4$][ClO$_4$] in MeCN solution at room temperature

Cyclic Voltammetry.—The redox chemistry of complexes **1** and **2** is characterized by the lack of reversible processes even at −40 °C. A representative voltammogram is depicted in Fig. 2 (for compound **2**). During a reductive potential sweep the wave A, without an associated anodic response regardless of the scan

Table 2 Redox potentials[a] (in V) for the technetium couples

	Tc^{III}–Tc^{II}		Tc^{III}–Tc^{IV}		Tc^{IV}–Tc^{V}		
Compounds	E_c	E_a	E_a	E_c	E_a	E_c	$E_a(Tc^{III}-Tc^{IV}) - E_c(Tc^{III}-Tc^{II})$
$[TcL^1{}_2(O{=}L^1)]$[b]	−2.122	—	0.162	—	0.588	—	2.284
$[TcL^2{}_2(O{=}L^2)]$[b]	−2.162	—	−0.012	—	0.318	—	2.15
$[TcL^3{}_3]$[c]	−0.694	−0.581	0.506	0.408	1.266	1.161	1.2

[a] Potentials are reported with respect to the ferrocenium–ferrocene couple. [b] Values measured at 0.200 V s^{-1}; the supporting electrolyte is 0.1 mol dm^{-3} $[NEt_4][ClO_4]$. [c] From ref. 11, recorded in CH_2Cl_2; the supporting electrolyte is 0.2 mol dm^{-3} $[NBu^n{}_4][BF_4]$.

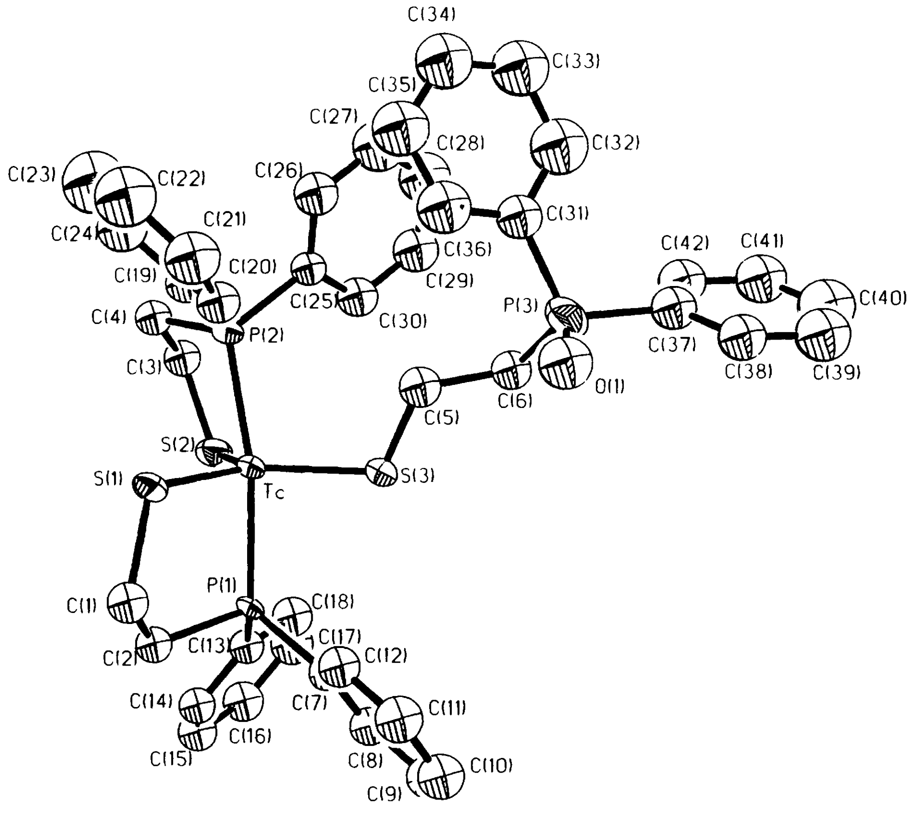

Fig. 3 An ORTEP view of complex **1**

rate, is indicative of a non-reversible process; moreover peak B (irreversible at scan rates from 0.050 to 0.600 V s^{-1}) appears during the potential backscan. In the anodic region waves C and D appear without a corresponding cathodic response, therefore this is attributable to a non-reversible process. Associated with peak C is the wave system E/F. Associated with peak D is the system G/H, which is peculiar to complex **2**. Experiments at differential potential scan rates indicate that peaks B, E/F and G/H originate from chemical reactions subsequent to irreversible reduction/oxidation of the starting complexes. Comparison with the ferrocenium–ferrocene couple, used as internal standard, and controlled-potential coulometries, establish that all the main charge transfers (peaks A, C and D) are one-electron processes. The value of the potentials (Table 2) show only small differences between the two complexes, but **2** is harder to reduce and easier to oxidize than is **1**, while the difference between the potentials indicates that **1** has a slightly wider stability range (by 134 mV). The pendant P=O unit present in both complexes **1** and **2** seems not to be involved in any of the described reduction waves. Indeed the voltammogram of the 'free oxidized' ligand does not show any corresponding wave in the cathodic region. The electrochemical results clearly establish for both **1** and **2** a larger range of redox stability with respect to complex **3**, however once reduced/oxidized both **1** and **2** undergo rapid chemical reactions.

Structure of Complex **1**.—An ORTEP[24] view of the complex **1** is shown in Fig. 3. Two L^1 moieties act as PS-bidentate donor ligands toward the Tc atom, being almost mutually orthogonal (99.5°) with bite angles approaching 90° (86.3 and 84.2°) (Table 3). This bidentate co-ordination results in two five-membered chelate rings which adopt an envelope conformation with C(2) and C(4) atoms deviating from the pertinent mean plane by 0.52 and 0.70 Å, respectively, the values of the S–C–C–P angles being 41.2 and 46.5°. The monodentate $Ph_2P(O)CH_2CH_2S^-$ ligand completes the co-ordination sphere and the distortion of the inner core from an ideal trigonal bipyramid is evidenced mainly by the P(1)–Tc–P(2) angle (169.9°), while the stereochemistry is not severely distorted in the equatorial S(1), S(2), S(3) plane [Tc deviates by 0.04 Å toward P(2) and maximum departure of 4.5° from the ideal 120° value for S–Tc–S angles]. The alkyl chain corresponding to the monodentate ligand is arranged in such a way that it is nearly fully extended, exhibiting *anti-anti* orientation of the torsion angles around S(3)–C(5) and C(6)–P(3) (−147.1, −153.4 and 178.0°, respectively) so maximizing the Tc ··· P(3) separation (6.23 Å). The P=O bond distance (1.51 Å) falls within the wide range (1.38–1.56 Å) encountered in many phosphoryl compounds[25] but it is slightly longer than the value observed in the parent compound $Ph_3P{=}O$ (1.46 Å).[26]. In the co-ordinated bidentate ligand, the two phenyl rings on the phosphorus atom are almost perpendicular to each other (dihedral angles of 93.7 and 95.8°, respectively), whereas in the monodentate one they are 120.7°. Table 4 summarizes Tc–P and Tc–S bond distances for the technetium(III) complexes containing both phosphine and thiolate ligands. The large range observed for these distances, from 2.273(2) to 2.510(5) Å for Tc–P and from 2.231(2) to 2.489(2) Å for Tc–S, reflects not only experimental errors, but primarily packing forces, structural *trans* effects and steric requirements of the ligands. The 17 Tc–P distances have an average value of 2.415 Å and a dispersion s of 0.059 Å, calculated from $[\Sigma(d_n - d)^2/(n - 1)]^{\frac{1}{2}}$. The same calculation restricted to the 12 Tc–P distances with *trans*-P influence results in an average of 2.420 Å and a dispersion of 0.021 Å. A similar analysis of Tc–S distances shows an average of 2.294 Å and a dispersion of 0.065 Å. However, close inspection of the eight Tc–S distances in octahedral technetium(III) complexes containing a S_2P_4 donor set, gives an average of 2.295 Å (s = 0.029 Å). This value seems to be practically insensitive to the *cis/trans* geometry of the complex and to the substituents at the donor moieties. Only two distances significantly deviate, up to 2.489(2) Å,[10] and they belong to the octahedral complexes containing a $S_3(\pi$ acceptor$)_3$ donor set. The reason for this lengthening may be attributable in principle to both steric and electronic factors, but the increased donor ability of the overall set, which takes a sulfur atom away from the metal to ensure an homogeneous electron-density distribution around the Tc^{III}, seems to play a crucial role (see below). Increasing the donor ability of the ligand from arene- to alkane-thiolate induces the complex to assume a trigonal-bipyramidal geometry with the sulfur donors occupying equatorial sites. This arrangement is quite common for transition-metal complexes containing two π-acceptor groups in the apical positions.[22] In the two trigonal-bipyramidal complexes reported in Table 4 the Tc–S mean distance contracts to 2.240 Å (s = 0.010 Å), a value pretty close to those found [from 2.234(6) to 2.265(4) Å] in the four thiolatotechnetium(III)[4,5] complexes containing π-acceptor groups rather than phosphines in the apical positions.

Table 3 Selected bond lengths (Å) and angles (°)

Tc–S(1)	2.232(5)	Tc–S(2)	2.245(4)
Tc–S(3)	2.256(3)	Tc–P(1)	2.392(3)
Tc–P(2)	2.379(3)	S(1)–C(1)	1.87(2)
S(2)–C(3)	1.85(1)	S(3)–C(5)	1.83(1)
P(1)–C(2)	1.82(2)	P(2)–C(4)	1.83(1)
C(1)–C(2)	1.49(2)	C(3)–C(4)	1.53(2)
C(5)–C(6)	1.52(2)	C(6)–P(3)	1.82(1)
P(3)–O(1)	1.51(2)	P(1)–C(7)	1.85(1)
P(1)–C(13)	1.86(1)	P(2)–C(19)	1.80(2)
P(2)–C(25)	1.87(2)	P(3)–C(31)	1.81(1)
P(3)–C(37)	1.82(2)		
S(1)–Tc–S(2)	116.6(1)	Tc–S(2)–C(3)	110.7(4)
S(2)–Tc–S(3)	124.7(2)	S(2)–C(3)–C(4)	110.6(10)
S(1)–Tc–S(3)	118.6(1)	P(2)–C(4)–C(3)	109.5(8)
S(1)–Tc–P(1)	86.3(1)	Tc–P(2)–C(4)	103.6(4)
S(2)–Tc–P(1)	90.2(1)	Tc–S(3)–C(5)	116.3(4)
S(3)–Tc–P(1)	90.2(1)	S(3)–C(5)–C(6)	112.8(8)
S(1)–Tc–P(2)	88.7(1)	P(3)–C(6)–C(5)	111.3(10)
S(2)–Tc–P(2)	84.2(1)	O(1)–P(3)–C(6)	111.3(7)
S(3)–Tc–P(2)	99.9(1)	C(6)–P(3)–C(31)	108.3(6)
P(1)–Tc–P(2)	169.9(1)	C(6)–P(3)–C(37)	104.5(7)
Tc–S(1)–C(1)	110.5(5)	O(1)–P(3)–C(31)	109.4(8)
S(1)–C(1)–C(2)	110.8(12)	O(1)–P(3)–C(37)	113.1(7)
P(1)–C(2)–C(1)	115.1(10)	C(31)–P(3)–C(37)	109.9(8)
Tc–P(1)–C(2)	103.9(4)	C(7)–P(1)–C(13)	102.7(5)
C(19)–P(2)–C(25)	102.5(6)		

In the molecular packing of the two molecules in the unit cell intermolecular contacts shorter than the sum of the van der Waals radii have not been observed.

Biodistribution Studies.—Preliminary results of the biodistribution studies in rats, accomplished by the procedure described elsewhere,[19] indicated that all three agents are invariably taken up by the liver according to their high lipophilic character and HPLC retention times, whereas the uptake in other organs is of little interest.

Stereochemistry.—Thiolate ligands are known to be effective σ donors and possible π donors as well.[22] Modification of the organic portion of the ^-SR group induces variation in the nucleophilic character of the sulfur atom along either a σ or π route (or both) yielding a wide class of slightly different ligands. In general, alkanethiols can be considered better nucleophiles than arenethiols, which in turn seem to exihibit some π-acid character (*i.e.* when they are just co-ordinated to the Tc^{III} [27]). It is also well established that phosphines are π-acceptor ligands;[15] this property is stronger for aryl- than for alkylphosphines,[28] which in turn are considered better σ donors. In addition, as a general feature, alkylphosphines are easier to oxidize than arylphosphines and, consequently, our monoalkyldiarylphosphines (HL^1 and HL^2) have a greater tendency to oxidize than does HL^3. Both phosphines and thiols are good reducing agents toward high-valent transition metals.[15,26] The mixed phosphine–thiols HL^n utilized in this work match the properties described above for separate monodentate phosphine and thiol ligands, indeed HL^n are good reductants with enhanced co-ordination ability by virtue of the chelate effect. Furthermore their donor/acceptor properties can be finely tuned by varying the substituents at both the ligating atoms, thus HL^3 exhibits the strongest π-acid character in the series, while the alkylphosphine–thiols HL^1 and HL^2 are better donors *via* both P and S and less strong π acceptors.[29] This class of ligands favours the obtainment of technetium(III) species.

The d^4 system is a very challenging electronic configuration in that it allows the synthesis of compounds exhibiting variable

Table 4 Comparison of the Tc–P and Tc–S bond distances in technetium(III) complexes containing both phosphine and thiolate ligands

Complex[a]	Co-ordination number	Geometry[b]	Tc–P/Å	Tc–S/Å	Ref.
trans-$[Tc(dmpe)_2(SMe)_2]^+$	6	*OC*	2.422(2), 2.434(2)	2.298(2), 2.302(2)	6
trans-$[Tc(depe)_2(SMe)_2]^+$	6	*OC*	2.440(1), 2.458(1)	2.302(1)	6
cis-$[Tc(dmpe)_2(SPh)_2]^+$	6	*OC*	2.409(5), 2.426(5), 2.467(6), 2.510(5)	2.277(5), 2.300(5)	8
$[Tc\{P(C_6H_4S\text{-}o)_3\}(CNPr^i)_2]$	6	*OC*	2.290(2)	2.310(2), 2.328(2), 2.390(2)	9
$[TcL^3_3]$	6	*OC*	2.406(1), 2.424(1), 2.477(1)	2.258(1), 2.297(1). 2.489(2)	10,11
$[Tc\{P(C_6H_4S\text{-}o)_3\}(CNPr^i)]$	5	*TBPY*	2.273(2)	2.231(2), 2.233(3), 2.245(3)	9
$[TcL^1_2(O{=}L^1)]$	5	*TBPY*	2.379(3), 2.392(3)	2.232(5), 2.245(4), 2.256(3)	This work

[a] dmpe = 1,2-bis(dimethylphosphino)ethane; depe = 1,2-bis(diethylphosphino)ethane. [b] *OC* = Octahedron, *TBPY* = trigonal bipyramid.

(different) co-ordination geometries. This tendency is even magnified when Tc^{III} is surrounded by sulfur and phosphorus donor atoms. In fact, five-, six- and seven-co-ordinated species are accessible depending on the combination of the ligating groups which stabilize trigonal-bipyramidal, octahedral and capped-octahedral arrangements.[1,30]

The novel five-co-ordinate phosphine–thiolato complexes $[TcL''_2(O{=}L'')]$ represent an example of neutral diamagnetic, 14-electron species which resemble a class of previously prepared trigonal-bipyramidal technetium(III) thiolato compounds of the type $[Tc(SR)_3Y_2]$ (Y = various neutral monodentate ligands; SR = sterically hindered arenethiolate ligand).[4,5] The sulfur atoms sit on the equatorial plane of the trigonal bipyramid and two π-acid groups occupy the axial positions; two of the aryl rings are consistently on the same side of the plane, while the other is on the opposite side. Such an arrangement allows incorporation of only small π-acid ligands in the more crowded axial position (*i.e.* MeCN or CO), whereas the opposite axial site is open to accept relatively more encumbered ligands such as pyridine or $CNPr^i$. In addition, the more sterically demanding PPh_3 has been found *trans* to MeCN in the complex $[Re(SPh)_3(MeCN)(PPh_3)]$, providing that all the phenyl rings of the thiolate groups are oriented on the opposite side with respect to the PPh_3 moiety.[31] By reducing the steric constraints by using less bulky monophosphines the *trans*-P configuration is attained as shown by $[Re(SPh)_3(PMe_2Ph)_2]$.[32] So, the S_3(π acceptor)$_2$ donor set will adopt a trigonal-bipyramidal environment and, by changing the steric demand of the ligand set, alternatively bulky thiolate and small π-acid groups or bulky π-acid and small thiolate groups can be accommodated around the metal(III) centre (M = Tc or Re). Thus, by reducing the bulk of R in the equatorial ^-SR thiolate moieties, *i.e.* by incorporating an aliphatic residue, bulkier π-accepting triphenylphosphine-like ligands can be placed in the *trans* axial sites, as evidenced in the $[TcL''_2(O{=}L'')]$ complexes. In this view, considering only steric factors, the obtainment of the octahedral *mer*-$[TcL^3_3]$ complex is quite surprising, the $^-L^3$ chelate undoubtedly being the more crowded ligand of the series. Moreover, an even bulkier HL^3-like chelate, which contains a trimethylsilyl substituent *ortho* to the thiolate group, affords the tris homoleptic rhenium(III) complex upon reaction with $[ReOCl_4]^-$ in alcohols.[33] On the other hand, the rigidity imposed by the geometry of the HL^3 chelate at the P and S atoms, similar to that of dithiolene ligands, favours the co-ordination of both donors. In addition, ligand steric factors determine the meridional configuration adopted by the bidentate ligand in order to minimize steric constraints among those six phenyl rings, which are attached to the phosphorus atoms and are not directly involved in the co-ordination. Even though electronic factors would favour the facial arrangement in $[TcL^3_3]$ since this would place three σ donors (sulfur) *trans* to three π acceptors (phosphorus), it turns out that the steric demand of the bulky HL^3 chelate is the primary factor in determining the final meridional configuration. It has to be noted, however, that the attainment of a six-co-ordinate species is made possible only through a severe distortion of the resulting octahedron. In particular, one bidentate ligand is remarkably weakly co-ordinated to the Tc^{III} causing the pertinent Tc–P and Tc–S distances to be 0.05 and 0.19 Å longer than in the other co-ordinated ligands. The dramatic lengthening of an individual Tc–S bond distance (that *trans* to another Tc–S linkage) can be explained by both the need of the overall molecule to expand its volume to accept three heavy sterically demanding ligands or in terms of a structural *trans* labilization operated by the thiolate group. By using HL^1 or HL^2 the increase in nucleophilicity at the thiolate donors by incorporating an alkyl chain between the P and S donor atoms, which reduces the steric demand of the ligands, induces the resulting technetium(III) complexes to rearrange to the trigonal-bipyramidal configuration. This strongly supports the electronic requirements as being the main factor responsible for the determination of the final arrangement in $[TcL''_2(O{=}L'')]$ (*n* = 1 or 2), no matter whether the pendant moiety bears an oxide terminal group.

Deutsch *et al.*[6–8] have synthesised a large number of octahedral $[M(SR)_2(L\text{–}L)_2]^+$ complexes (M = Tc or Re; R = alkyl or aryl; L–L = diphosphine such as $R'_2PCH_2CH_2PR'_2$, R = Me, Et or Ph) and both *cis* and *trans* isomers can be isolated. A close inspection of this class of complexes revealed that *cis* isomers can only be synthesised when the less bulky dmpe ($Me_2PCH_2CH_2PMe_2$) ligand is utilized, which can be comfortably situated *cis*. In addition, this arrangement is preferred if bulky arenethiolate groups complete the co-ordination sphere in order to minimize the steric strain associated with the M–S–C bond angles in the thiolato region. The authors conclude that in the synthesis of $[M(SR)_2(L\text{–}L)_2]^+$ complexes the main driving force for determining isomer formation appears to be a balance between diphosphine-ligand steric requirements and thiolate ligand steric requirements while electronic factors make a marginal contribution.[34] Totally consistent steric arguments can be made to explain the *cis* geometry exhibited by the six-co-ordinated $[Tc(SPh)_2(ttod)]^+$ complex where ttod (5,8,11,14-tetrathiaoctadecane) represents a tetrathioether ligand of low steric demand.[35] From the electronic point of view, the S_2Y_4 (Y = P or $S_{thioether}$) co-ordinating set appears to be a particularly well suited donor/acceptor system for Tc^{III} in octahedral $[Tc(SR)_2(L\text{–}L)_2]^+$ and $[Tc(SPh)_2(ttod)]^+$ complexes. In fact, within these complexes the nucleophilicity of the thiolate groups is sufficiently balanced by the acidity of the diphosphine (or tetrathioether) chelates and, moreover, the availability of a number of acceptor sites also makes the reduced technetium(II) species easily accessible. Replacement of a phosphorus donor for a sulfur thiolate donor to give the S_3P_3 set present in the *mer*-$[TcL^3_3]$ derivative causes the Tc^{III} to experience an increased overall electron density. The metal is still able to accommodate three bidentate ligands, but the resulting complex is highly distorted from ideal octahedral geometry (see above). It appears that upon co-ordination of the aromatic bidentate chelate the intraligand delocalization of the electron density by conjugation through the five-membered chelate rings allows the octahedral configuration to be retained. In fact, when the effect of conjugation is removed by incorporating an alkyl chain between the P and S donors of the ligand, the Tc^{III} is no longer able to tolerate the donor strength of three alkanethiolate groups in a six-co-ordinated environment and rearranges to the more thermodynamically stable trigonal-bipyramidal configuration in order to maximize sulfur donation to the metal and maximize π-back donation from the metal to the axial ligands. From the stereochemical point of view, consistent results are obtained upon reaction of suitable rhenium precursors with the PS_2-tridentate phosphine–thiol ligands. The aromatic chelate 2-(phenylphosphino)bisbenzenethiol gives a neutral six-co-ordinate rhenium(IV) species,[33] which contains two chelates completely co-ordinated to the metal. Conversely, the aliphatic version, namely 3-phenyl-3-phosphapentane-1,5-dithiol, affords a five-co-ordinate rhenium(III) complex with apical phosphorus, three thiolate donors on the equatorial plane and a pendant SH group.[13]

Conclusion

Mixed bidentate phosphine–thiolate ligands HL^n readily react with $[TcO_4]^-$ or $[TcOCl_4]^-$ to give neutral and stable technetium(III) complexes, the geometry of which is dependent on the nature of the carbon chain interposed between the P and S donor. Trigonal-bipyramidal and distorted-octahedral arrangements are accessible for alkyl- and aryl-phosphine–thiolate chelates, respectively. The five-co-ordinate compounds show a wide range of redox stability (> 2.00 V) in the 3+ oxidation state. The occurrence of two co-ordination geometries seems to be ascribed primarily to electronic factors which govern the metal–donor interactions. PS-Bidentate ligands which possess the strongest donor properties in the investigated series, even if less sterically demanding, favour the formation of less-crowded trigonal-bipyramidal species, while more bulky PS-bidentate ligands which allow intraligand electron-density delocalization favour the formation of more crowded octahedral derivatives. Therefore, in technetium(III) complexes containing phosphine and thiolate or mixed phosphine–thiolate ligands, the ligand donor/acceptor properties appear to be predominant in establishing the co-ordination sphere, *i.e.* S_3P_3 or S_3P_2, while ligand steric requirements appear to be predominant in determining the stereochemistry of the resulting complexes within a well fixed co-ordinating atom set, *i.e.* octahedral *cis* or *trans* arrangement in S_2P_4 systems, octahedral *mer* or *fac* arrangement in S_3P_3 systems.

Experimental

Physical Measurements.—Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser. The IR spectra were recorded on a Mattson 3030 Fourier-transform spectrometer (4000–350 cm^{-1}) using Nujol mulls between CsI disks, ^1H and ^{31}P NMR spectra and magnetic susceptibility measurements (Evans method[36]) on a Bruker AC-200 instrument, using $SiMe_4$ (^1H spectra) as internal reference and 85% aqueous H_3PO_4 (^{31}P spectra) as external reference. The UV/VIS spectra were recorded in CH_2Cl_2 using a Cary 17D spectrophotometer (700–250 nm). Conductivity measurements were made at 25 °C using a Metrohm Herison E518 conductometer. Fast-atom bombardment (FAB) mass spectra in the positive mode were recorded by using a glycerol matrix on a VG 30–250 spectrometer (VG Instrument) at the probe temperature. Xenon was used as the primary beam gas, and the ion gun was operated at 8 keV (*ca.* 1.28×10^{-15} J) and 100 μA. The data were collected over the mass range m/z 100–1000 at 0.7 s per scan. Chromatographic data were collected on a HP 1090 instrument connected with a HP 3390A integrator using a diode-array UV/VIS detector or alternatively a γ-detector. Cyclic voltammetry measurements were performed on a BAS (Bioanalytical System Inc.) CV-IB cyclic voltammograph either at room temperature or at −40 °C in liquid nitrogen–acetone slurries, under an atmosphere of nitrogen, using a conventional three-electrode cell. A platinum-disk electrode (area *ca.* 10^{-3} cm^2) was used as the working electrode, a platinum wire as the counter electrode and a saturated calomel reference electrode (SCE). Controlled-potential coulometry was performed with an AMEL model 721 integrator and the following electrodes: platinum-spiral wire working electrode, platinum-auxiliary foil electrode isolated inside a salt bridge by a medium-glass frit, and an SCE. The measurements were done in dry and degassed MeCN (Aldrich gold label solvent) with 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ as the supporting electrolyte. Potentials of the cyclic voltammetric waveform were scanned at 0.2 V cm^{-1} and were referenced internally to the ferrocenium–ferrocene couple.[37] **CAUTION**: ^{99}Tc is a weak β-emitter (E_{max} = 0.292 MeV, *ca.* 4.67×10^{-17} J) with $t_{\frac{1}{2}} = 2.12 \times 10^5$ years. Handling of this material was carried out in laboratories approved for low-level radioactivity using glove-boxes under moderate vacuum for the synthesis and recovery operations. Technetium-99m is a γ-emitter (E_γ = 0.142 MeV, *ca.* 2.27×10^{-17} J) with $t_{\frac{1}{2}}$ = 6.02 h. Handling of this isotope requires adequate lead shielding when mCi amounts are utilized.

Materials.—Unless otherwise stated, all chemicals were of reagent grade. Technetium-99, as $[NH_4][TcO_4]$ in 0.1 mol dm^{-3} ammonia solution, was obtained from the Radiochemical Centre, Amersham. The salts $[NBu^n{}_4][TcOCl_4]$ and $[TcCl_3(MeCN)(PPh_3)_2]$ were prepared according to the literature methods.[38] Technetium-99m was eluted as $Na[^{99m}TcO_4]$ from a $^{99}Mo/^{99m}Tc$ commercial generator (Sorin Biomedica S.p.A.) in 0.9% aqueous NaCl solution.

Table 5 Structure determination summary for complex **1**

Empirical formula	$C_{42}H_{42}OP_3S_3Tc$
M	851.9
Colour, habit	Purple-red, parallelopiped
Crystal size (mm)	0.08 × 0.24 × 0.08
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.991(4)
b/Å	12.417(4)
c/Å	18.687(8)
α/°	73.37(3)
β/°	76.88(3)
γ/°	73.68(3)
U/Å^3	2104.4(15)
Z	2
D_c/Mg m^{-3}	1.344
μ/mm^{-1}	0.618
F(000)	876
Diffractometer	Siemens R3m/V
Radiation	Mo-Kα (λ = 0.710 73 Å)
T/K	294
Monochromator	Highly oriented graphite crystal
2θ Range/°	4.0–45.0
Scan type	ω–2θ
Scan speed	Variable, 3.97–14.65° min^{-1} in ω
Scan range (ω/°)	0.65 plus Kα separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	2 every 100
Index ranges	$0 < h < 6, -12 < k < 13, -19 < l < 20$
Independent reflections	4647
Observed reflections	2765 [$F > 4.0\sigma(F)$]
System used	Siemens SHELXTL PLUS[40]
Solution	Heavy-atom method
Refinement	Full-matrix least squares
Quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ (w = 1)
Number of parameters refined	238
Final R indices	R = 0.0703 (observed data), R = 0.1165 (all data)
Goodness-of-fit	0.84
Data-to-parameter ratio	11.6:1
Largest difference peak/e Å^{-3}	1.02 (1.1 Å from Tc)
Largest difference hole/e Å^{-3}	−1.07

Preparation of the Ligands.—The compounds HL^1 and HL^2 were prepared by Argus Chemicals according to the method reported by Blower *et al.*[13] (for HL^2, ethylene sulfide was replaced by propylene sulfide), while HL^3 was prepared as described elsewhere.[10] Both HL^1 and HL^2 are air sensitive, thus they were stored under an inert atmosphere and all the reactions and manipulations were routinely performed under a nitrogen atmosphere with standard Schlenk-tube techniques.

Preparation of Technetium-99 Complexes.—$[TcL^1{}_2(O{=}L^1)]$ **1**. Solid $[NH_4][TcO_4]$ (42 mg, 0.23 mmol) was suspended in degassed EtOH (10 cm^3) and CH_2Cl_2 (1 cm^3), and the mixture was further degassed by a nitrogen flux for 3 min. Liquid HL^1 (285 mg, 1.15 mmol) was quickly added by syringe whilst stirring at room temperature, and the solution immediately became red. It was then refluxed for 0.5 h under a nitrogen atmosphere giving a red-cyclamen clear solution. After cooling and concentration (by a nitrogen flow) to about 5 cm^3, a red-cyclamen solid appeared which was filtered off, washed with EtOH (3 × 1 cm^3) and dried under vacuum. Yield 183 mg, 94% (Found: C, 59.0; H, 5.2; S, 12.1. $C_{42}H_{42}OP_3S_3Tc$ requires C, 59.3; H, 4.9; S, 11.3%). Complex **1** is soluble in CH_2Cl_2, $CHCl_3$,

Table 6 Atomic coordinates ($\times 10^4$) for complex **1**

Atom	*x*	*y*	*z*
Tc	7 632(1)	6 703(1)	6 066(1)
S(1)	9 571(4)	6 425(3)	6 561(2)
S(2)	7 914(4)	6 009(2)	5 043(2)
S(3)	5 578(4)	7 734(3)	6 576(2)
P(1)	8 224(4)	8 449(2)	5 276(2)
P(2)	7 434(4)	4 803(2)	6 750(2)
P(3)	2 355(5)	7 205(3)	8 580(2)
O(1)	2 941(13)	7 852(9)	8 961(6)
C(1)	10 417(17)	7 675(11)	6 139(7)
C(2)	10 054(15)	8 277(10)	5 369(6)
C(3)	8 008(17)	4 439(10)	5 320(6)
C(4)	8 455(15)	3 906(9)	6 098(6)
C(5)	4 730(15)	7 006(10)	7 488(6)
C(6)	3 129(17)	7 374(11)	7 586(7)
C(7)	7 360(15)	9 839(10)	5 545(6)
C(8)	6 744(16)	10 820(10)	5 039(7)
C(9)	6 191(17)	11 862(11)	5 257(7)
C(10)	6 183(17)	11 893(12)	5 955(7)
C(11)	6 713(18)	10 933(12)	6 472(8)
C(12)	7 297(16)	9 919(11)	6 259(7)
C(13)	8 267(16)	8 852(10)	4 236(6)
C(14)	9 380(16)	9 294(10)	3 754(6)
C(15)	9 381(18)	9 587(11)	2 991(7)
C(16)	8 320(18)	9 466(11)	2 701(8)
C(17)	7 196(20)	9 044(13)	3 188(8)
C(18)	7 206(18)	8 752(11)	3 946(7)
C(19)	8 103(16)	4 122(10)	7 629(7)
C(20)	7 849(18)	4 746(12)	8 165(8)
C(21)	8 313(20)	4 280(14)	8 864(9)
C(22)	9 007(23)	3 142(17)	9 018(12)
C(23)	9 346(24)	2 570(18)	8 493(11)
C(24)	8 884(19)	3 004(13)	7 791(9)
C(25)	5 679(16)	4 432(10)	6 954(7)
C(26)	5 346(19)	3 592(12)	7 562(8)
C(27)	4 003(23)	3 317(16)	7 672(11)
C(28)	3 106(25)	3 896(15)	7 175(10)
C(29)	3 445(21)	4 735(13)	6 564(9)
C(30)	4 757(19)	5 017(12)	6 444(8)
C(31)	2 750(20)	5 681(12)	9 040(8)
C(32)	1 737(22)	5 005(15)	9 220(9)
C(33)	2 092(23)	3 847(15)	9 606(9)
C(34)	3 375(23)	3 354(16)	9 736(9)
C(35)	4 406(24)	3 973(15)	9 562(9)
C(36)	4 034(21)	5 171(14)	9 218(8)
C(37)	458(18)	7 736(12)	8 575(8)
C(38)	−211(19)	8 646(12)	8 972(8)
C(39)	−1 660(22)	9 100(15)	8 935(9)
C(40)	−2 334(25)	8 715(16)	8 528(10)
C(41)	−1 695(21)	7 878(13)	8 157(9)
C(42)	−277(19)	7 391(12)	8 197(8)

Me_2CO, MeCN, and dimethylformamide (dmf), slightly soluble in MeOH, EtOH, Et_2O, and insoluble in water and hydrocarbons. Molar conductivity in MeCN: $\Lambda_M = 10.7$ ohm^{-1} cm^2 mol^{-1}. FAB mass spectrum: *m/z* 851 ($[M]^+$, 42), 835 ($[M - O]^+$, 16), 621 ($[M - L^1 + O]^+$, 100) and 605 ($[M - L^1]^+$, 24%). UV/VIS bands: λ_{max}/nm 540 (ε/dm^3 mol^{-1} cm^{-1} = 2400), 490 (2000), 365 (6100), 330 (5700) and 295 (19 300). IR($\tilde{v}$/cm^{-1}, major bands): 1434vs, 1101s (P=O), 815s, 743vs, 696vs, 516vs, 499vs, 420s and 410s. NMR ($CDCl_3$): ^1H (200 MHz, standard $SiMe_4$), δ 7.6–7.0 (30 H, m, aryl protons) and 3.10–1.90 (12 H, 4 overlapped m, methylene protons); ^{31}P (81.01 MHz, standard 85% H_3PO_4), δ 69.9 (m, TcP) and 27.7 (s, P=O). Crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2–EtOH solution at 4 °C.

$[TcL^2_2(O{=}L^2)]$ **2**. This complex was prepared according to the procedure described above for **1**, however the crude violet solid collected after filtration was recrystallized from a CH_2Cl_2–MeOH solution giving a lilac powder which was washed with MeOH (2 × 1 cm^3) and dried under vacuum. Yield 84% (Found: C, 60.2; H, 5.6; S, 11.2. $C_{45}H_{48}OP_3S_3Tc$ requires C, 60.5; H, 5.4; S, 10.8%). Complex **2** is soluble in CH_2Cl_2, $CHCl_3$, Me_2CO, MeCN and dmf, slightly soluble in MeOH and EtOH, and insoluble in water and hydrocarbons; Et_2O solubilizes the complex, but decomposition with time occurs. Molar conductivity in MeCN: $\Lambda_M = 15.2$ ohm^{-1} cm^2 mol^{-1}. FAB mass spectrum: *m/z* 893 ($[M]^+$, 67), 649 ($[M - L^2 + O]^+$, 100) and 633 ($[M - L^2]^+$, 78%). UV/VIS bands: λ_{max}/nm 550 (ε/dm^3 mol^{-1} cm^{-1} = 1000), 490 (1200), 370 (4100), 335 (sh) and 295 nm (10 200). IR ($\tilde{v}$/cm^{-1}, major bands): 1434vs, 1094vs (P=O), 741vs, 696vs, 516s, 490s and 379w. NMR ($CDCl_3$): ^1H (200 MHz, standard $SiMe_4$), δ 7.9–7.1 (30 H, m, aryl protons) and 3.00–1.50 (18 H, unresolved m, methylene protons); ^{31}P (81.01 MHz, standard 85% H_3PO_4), δ 22.4 (m, TcP) and 31.4 (s, P=O).

Both complexes **1** and **2** can also be prepared from $[NBu^n_4][TcOCl_4]$ using a 1 : 3 (Tc : L^n) stoichiometric ratio in CH_2Cl_2–EtOH (1 : 10 v/v) at room temperature. Average yields 90%.

$[TcL^3_3]$ **3**. This complex was prepared according to the procedure reported in ref. 10. ^1H NMR ($CDCl_3$): set of resonances in the δ 8.2–6.2 region and a broad singlet centred at δ 13.0. Susceptibility measurements in dichloromethane solution gave $\mu = 2.3\ \mu_B$.

*Preparation of Technetium-*99*m Complexes.*—Technetium-99m complexes were prepared by different routes depending on the nature of the HL^n ligand and under anaerobic conditions.

With HL^1 *and* HL^2. In a vial (5 cm^3) containing $Na[^{99m}TcO_4]$ (0.1 cm^3, about 2 mCi of $[^{99m}TcO_4]^-$), which had been eluted from a commercial $^{99}Mo/^{99m}Tc$ generator with physiological saline. To this was added EtOH (0.5 cm^3), and the solution was degassed by a nitrogen flux for 5 min. After addition of neat HL^1 or HL^2 (7 × 10^{-3} cm^3), the vial was sealed under nitrogen and heated in a paraffin-oil bath at 75 °C for 1 h.

With HL^3. A vial (5 cm^3) containing an ethanolic solution (1.5 cm^3) of HL^3 (2 × 10^{-3} mol dm^{-3}), $Na[^{99m}TcO_4]$ (0.3 cm^3, about 5 mCi of $[^{99m}TcO_4]^-$) and CF_3CO_2H (0.01 cm^3) in water (1 : 10, v/v) was sealed under nitrogen and heated in a paraffin oil bath at 90 °C for 45 min. Radiochemical analyses, accomplished by HPLC with radiometric detection, show yields of the $[^{99m}TcL^n_3]$ compounds to be consistently over 90% with 85–90% of the injected activity generally recovered in the eluate. The three technetium complexes exhibit different retention times on a reversed-phase C_{18} column upon elution at a flow rate of 1 cm^3 min^{-1} and the mobile phases MeCN (72), thf (15) and 5 × 10^{-3} mol dm^{-3} NH_4O_2CMe in water (buffer) (13%): **1**, 4.04; **2**, 4.66; **3**, 7.89 min. The retention times of the 'no carrier added'[39] ^{99m}Tc reaction mixture were compared to those exhibited by the ^{99}Tc-containing complexes prepared using mg amounts of ^{99}Tc and found to be identical. In addition, 'carrier added' experiments, accomplished as previously described,[19] confirmed the identity of the molecular structure of both ^{99}Tc- and ^{99m}Tc-containing complexes. Crude $[^{99m}TcL^1_2\ (O{=}L^1)]$ and $[^{99m}TcL^2_2\ (O{=}L^2)]$ were injected in rats, while $[^{99m}TcL^3_3]$, prior to use, was purified, from excess of ligand, by the following procedure: (*i*) the crude preparation was diluted with physiological saline to yield a final water–EtOH (70 : 30 v/v) clear solution, (*ii*) a Sep-Pak C_{18} cartridge (Waters) previously activated with an identical water–EtOH mixture was loaded with the diluted solution, (*iii*) water (10 cm^3) followed by water–EtOH (60 : 40 v/v) (20 cm^3) were used to wash the column, (*iv*) finally, the $[^{99m}TcL^3_3]$ was eluted from the cartridge with EtOH (2 × 0.5 cm^3) and the second aliquot was used for animal studies. Before evaluation *in vivo*, aliquots of the radiopharmaceutical solutions were again tested by HPLC to check the stability of the complexes.

Crystallography.—Several specimens of complex **1** were examined, and, while of appropriate size, were found invariably of poor habit, being split or broken. Details of crystal data, measurements of intensity and data processing are summarized in Table 5. No correction for absorption was made since rotation of the crystal at $\chi = 90°$ showed only a 5% variation in intensity of a reflection coincident with the φ axis of the diffractometer. Final fractional atomic coordinates and thermal parameters are given in Table 6, selected bond lengths and angles in Table 3. The quality of the refinement is low, as evidenced by the *R* value. We attribute this to the poor crystal quality, as also indicated by the high value of *R* (0.08) for equivalent (0*kl*) reflections, and the rather low ratio of observed to unique reflections (0.6 : 1). Despite data being collected from several crystals, they were of low quality and only allowed for anisotropic refinement of the Tc, S and P heavy atoms (238 parameters for 2765 observed reflections).

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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